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PILOT PLANT TREATMENT OF ACID MINE DRAINAGE BY REVERSE OSMOSIS

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Studies were conducted at the EPA Crown Mine Drainage Control Field Site (a) to reexamine the performance of a 227,000 lpd (60,000 gpd) reverse osmosis (RO) unit at recovery levels of 50 percent through 90 percent for a variety of dominantly ferrous iron acid mine drainage (AMD) feed qualities, (b) to evaluate the feasibility of using the neutrolosis process to treat AMD, and (c) to determine the AMD treatment capability of a coupled 18.9 lpm (5 gpm) sodium cycle cation exchange (CIX)/RO system.

Neutrolosis studies were conducted using both 227,000 lpg (60,000 gpd) and 15,100 lpd (4,000 gpd) spiral-wound membrane module RO units utilizing lime, soda ash, and lime-soda ash combinations as the neutralizing agents. The neutrolosis process did not increase system recovery beyond the maximum recovery levels attainable by once-through RO treatment of AMD. Precipitate fouling and osmotic pressure phenomena associated with neutrolosis caused an increased frequency of system operational and shutdown problems.

Using the coupled CIX/RO system, a greater than 90 percent recovery operation was achieved by the RO unit when the AMD feed was pretreated by the CIX unit.

This report represents the second phase of RO process research pertinent to AMD treatment at the EPA Crown Mine Drainage Control Field Site in fulfillment of Contract Number 68-03-0245 by West Virginia University under the sponsorship of the U. S. Environmental Protection Agency. This report covers the period May 1973 to November 1975.

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FOREWARD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report documents the results of pilot plant research conducted to both demonstrate and evaluate the applicability of reverse osmosis (RO)-based processes for treatment of acid mine drainage (AMD). The major processes considered are (a) a 227,000 liters per day (lpd) [60,000 gallons per day (gpd)] spiral-wound, RO unit; (b) lime, soda ash, and combined lime/soda ash neutrolosis processes; and (c) a coupled cation exchange (CIX)/RO treatment system. This work represents the second phase of RO process research pertinent to AMD treatment at the U. S. Environmental Protection Agency (EPA) Crown Mine Drainage Control Field Site. The first phase incorporated design, construction, and shake-down operations of the 227,000 lpd RO pilot plant facility. The third and final phase of the work will focus on the development of a state-of-the-art report/manual of practice for RO purification of mine drainage. Research and engineering personnel can use the results of this report as a basis for further investigations and/or design of AMD treatment systems utilizing both RO and coupled CIX/RO processes.

Additional information on this subject can be obtained by contacting the Energy Pollution Control Division of IERL-Ci.

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ABSTRACT

Studies were conducted at the EPA Crown Mine Drainage Control Field Site (a) to examine the performance of a 227,000 lpd (60,000 gpd) reverse osmosis (RO) RO unit at recovery levels of 50 percent through 90 percent for a variety of dominantly ferrous iron AMD feed qualities; (b) to evaluate the feasibility of using the neutrolosis (combination of RO and neutralization) process to treat AMD; and (c) to determine the AMD treatment capability of a coupled 18.9 lpm (5 gpm) sodium cycle (cation exchange/RO) CIX/RO system.

Neutrolosis studies were conducted using both 227,000 lpd (60,000 gpd) and 15,100 lpd (4,000 gpd) spiral-wound membrane module RO unit utilizing lime, soda ash, and lime-soda ash combinations as the neutralizing agents. The neutrolosis process did not increase system recovery beyond the maximum recovery levels attainable by once-through RO treatment of AMD. In addition, precipitate fouling and osmotic pressure phenomena associated with neutrolosis operations caused an increased frequency of system operational and shutdown problems.

Using the coupled CIX/RO system, greater than 90 percent recovery was achieved by the RO unit when the AMD feed was pretreated by the CIX unit.

This report represents the second phase of RO process research pertinent to AMD treatment at the EPA Crown Mine Drainage Control Field Site in fulfillment of Contract Number 68-03-0245 by West Virginia University under the sponsorship of the U.S. Environmental Protection Agency. The report covers work performed during the period from May 1973 to November 1975.

CONTENTS

Foreward iii

Abstract iv

Figures vi

Tables viii

Acknowledgments ix

1. Introduction 1
2. Conclusions 3
3. Recommendations 5
4. Background 6
    - Acid mine drainage treatment by reverse osmosis 6
    - Acid mine drainage treatment by ion exchange 9
    - Effect of ion exchange pretreatment on other processes . . 11
5. Description of the Pilot Plant Facility 14
    - 60K reverse osmosis system 14
    - 4K reverse osmosis system 30
    - Twin-bed ion exchange system 35
    - Neutralization systems 37
6. Reverse Osmosis Systems Operations 40
    - Principles of reverse osmosis 40
    - Results of experimental studies 43
    - Summary of operations and maintenance experiences - 60K RO unit 58
7. Coupled Reverse Osmosis/Neutralization Studies 60
    - Lime neutrolosis 60
    - Soda ash neutrolosis 71
    - Combined lime-soda ash neutrolosis 78
8. Coupled Cation Exchange/Reverse Osmosis AMD Treatment Systems 84
    - The cation exchange process 84
    - The coupled cation exchange/reverse osmosis process 87
    - Experimental procedures and results 87
    - Summary 105

References 108

Appendices

A. Chemistry Analyses for 60K RO Unit Operations (60-90 percent recovery) 111
B. Neutrolosis Process Model 115
    - Model derivation 115
    - Model utilization 124

FIGURES

Number		Page
1	AMD pilot plant facility building - Crown, WV	15
2	AMD bore hole pump - Crown, WV	19
3	9500 liter (2500 gallon) AMD holding tank	20
4	Pretreatment and product storage and blending assembly (60K RO unit)	21
5	Membrane-module pressure vessels and high pressure pump assembly (60K RO unit)	22
6	Sampling and pressure measurement assembly and instrument console (60K RO unit)	24
7	RO waste brine neutralization system	25
8	Crown mine drainage control field site sludge settling pond (west end view)	26
9	Crown mine drainage control field site sludge settling pond (east end view)	27
10	Process flowsheet - 60K RO unit at 50 percent recovery (8-6 pressure vessel array)	28
11	Membrane-module pressure vessels, sampling and pressure measurement assembly, and instrument console (4K RO unit)	34
12	Twin-bed CIX system	36
13	7600 liter (2000 gallon) outdoor surface aerator	38
14	37,900 liter (10,000 gallon) outdoor clarifier	39
15	Flux behavior of 60K RO unit at various recovery levels (tubes 1-7)	49
16	Flux behavior of 60K RO unit at various recovery levels (tubes 8-14)	50
17	Brine conductivity fouling studies - 4K RO unit	52
18	Flux comparison - tubes 1 and 2, CL-14 test	54
19	Flux comparison - tube 3, CL-14 test	54
20	Flux comparison - tubes 1 and 2, CL-50 test	55
21	Flux comparison - tube 3, CL-50 test	55
22	Flux comparison - tubes 1 and 2, L-39 test (5 mg/l)	56
23	Flux comparison - tube 3, L-39 test (5 mg/l)	56
24	Flux comparison - tubes 1 and 2, L-39 test (10 mg/l)	57
25	Flux comparison - tube 3, L-39 test (10 mg/l)	57
26	Process schematic for lime neutrolosis studies	62
27	60K RO unit product flux in last tube bank for tap water neutrolosis study at pH 11	70
28	60K RO unit product flux in last tube bank for Crown AMD lime neutrolosis study at pH 8	71
29	Flowsheet for "open loop" soda ash neutrolosis study	75
30	4K RO unit product fluxes for "open loop" soda ash neutrolosis study	77
31	60K RO unit product flux in last tube bank for "closed loop" soda ash neutrolosis study	80
32	Flowsheet for "open loop" lime-soda ash neutrolosis study	82
33	4K RO unit product fluxes for "open loop" lime-soda ash neutrolosis study	83

Number **Page**

34 AMD loading factor versus time. 89
35 FMA versus time in the CIX effluent 90
36 Calcium leakage profile 92
37 Magnesium leakage profile 93
38 Total hardness leakage profile. 94
39 Effect of salt dosage on resin capacity 95
40 Effect of salt dosage on regenerant utilization 96
41 Flowsheet of the coupled IX-RO system at 26.7°C (80°F) operating at 91.3% recovery (P/SF). 99
42 Effect of Na_2SO_4 waste brine on the total hardness leakage profile 102
43 Effect of salt dosage on calcium, magnesium, and total hardness leakages 103
B-1 Process schematic for analysis of the neutrolosis process . . . 116
B-2 $CaSO_4$ saturation factor versus once-through RO recovery 121
B-3 Lime neutrolosis treatment of Crown AMD to pH 11. 122
B-4 Lime neutrolosis treatment of Norton-type AMD to pH 11. 123

TABLES

Number		Page
1	60K RO Pressure Vessel Configurations.	30
2	Estimated Flows and Ratios of Brine to Product for Various Recovery Levels -- 60K RO Unit	31
3	Operations Summary for 60K RO Unit Shakedown Run @ 184 Hours (49.0 Percent Unit Recovery)	45
4	Water Permeability Coefficients (A_1) for Banks #1 and #2, 60K RO Unit Shakedown Run @ 184 Hours.	46
5	Chemistry Analysis for 60K RO Unit Shakedown Run @ 184 Hours .	46
6	Flow Rates for 60K RO Unit Operations (60 - 90 Percent Recovery).	48
7	Chemistry Analysis for Lime Neutralization of 60K RO Unit Brine at 75 Percent Unit Recovery.	67
8	Chemistry Analysis for Tap Water Lime Neutrolosis Study (pH 11) Day 2.	69
9	Chemistry Analysis for Tap Water Lime Neutrolosis Study (pH 11) Day 4.	69
10	Chemistry and Operational Data: Crown AMD Lime Neutrolosis Study (pH 8)	71
11	Chemistry Analysis for "Open Loop" Study, Hours 1-14, (Blended Raw AMD and Supernatant Feed)	76
12	Chemistry Analysis for "Open Loop" Study, Hours 14-18, (Supernatant Feed Only).	76
13	Chemistry Analysis for "Closed Loop" Soda Ash Neutrolosis. . .	79
14	Operating Conditions of the Ion Exchange System.	87
15	Average Composition of Crown AMD During 100 Day Period, 5/25/75 to 9/2/75.	88
16	Capacity and Regenerant Utilization Data	97
17	Representative Chemistry Analysis at a Salt Dosage of 240 kg/m^3 (15 lb/ft^3).	100
18	Comparison of Capacity and Regenerant Utilization at Different Salt Dosages	105
A-1	59.7 Percent Unit Recovery	111
A-2	69.6 Percent Unit Recovery	112
A-3	73.6 Percent Unit Recovery (7-4-3 Array)	112
A-4	73.6 Percent Unit Recovery (5-4-3-2 Array)	113
A-5	80.0 Percent Unit Recovery	113
A-6	85.4 Percent Unit Recovery	114
A-7	90.3 Percent Unit Recovery	114
B-1	Ksp Values	120

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SECTION 1

INTRODUCTION

The discharge of AMD emanating from both active and abandoned coal mines throughout the coal-producing areas in the United States has resulted in a serious water pollution problem since the first coal mining operation in Pennsylvania was begun in 1761. The problem is especially present in the Appalachian region, where acid mine discharges have contaminated many fresh-water streams and have diminished the available water supplies. As a result, the control of this serious problem has become a regional as well as national concern.

The formation of AMD is principally due to oxidation of iron sulfide minerals (pyrite or marcasite) that are found in coal seams. After coal is mined, the FeS_2 is oxidized in the presence of air and dissolved by water to form ferrous sulfate and sulfuric acid. Further oxidation of the ferrous sulfates produces ferric sulfate. Then, through subsequent hydrolysis, more sulfuric acid is produced along with the formation of ferric hydroxide. Therefore, a large quantity of iron sulfate is present in the AMD, and the sulfuric acid formed decreases the pH value of the acid mine water. This wastewater infiltrates surface waters and other ground waters, thus lowering the pH and increasing their dissolved solids content. However, the resulting pH is generally high enough to cause the precipitation of ferric hydroxide, which in turn deposits in stream beds and aquifiers and increases the turbidity of the water. The acid mine water also abounds in other metallic pollutants, such as aluminum, manganese, calcium and magnesium. Moreover, it is found that the relative pollutant concentrations and the temperature of AMD vary considerably with climatic conditions, and the extent to which acid mine waters become a source of pollution is also variable in different coal mining areas.

Although various neutralization treatment schemes can provide effluents of sufficient quality to meet discharge standards into natural waterways, they normally do not produce potable water. The purpose of studies conducted by West Virginia University has been the pilot-plant investigation of both RO and coupled cation exchange (CIX/RO) processes that do have the potential of yielding potable water from AMD.

This report represents the results of both analytical and experimental work conducted during the period May 1973 through November 1975 concerning treatment of AMD by RO-and CIX-based techniques to produce a high quality product water. The basic studies have involved pilot-plant scale operations at the EPA Crown Mine Drainage Control Field Site, Rivesville, West Virginia, and focused on:

- Evaluation of the operating performance of a 227,000 lpd (60,000 gpd) rated product output RO unit, containing spiral-wound cellulose acetate membrane modules, in terms of its ability to treat AMD at unit recoveries of 50 to 90 percent.
- Determination of the feasibility of using lime, soda ash, and combined lime-soda ash neutrolosis (combination RO/neutralization) processes to treat AMD focusing on enhanced overall systems and low-volume waste yields.
- Examination of coupled sodium cycle co-current CIX/RO systems as a potentially high recovery AMD treatment process.

SECTION 2

CONCLUSIONS

The following major conclusions are based on the results of the investigations of RO-based AMD treatment techniques conducted on ferrous mine discharge waters at the EPA Crown Mine Drainage Control Field Site, Rivesville, West Virginia:

- The 227,000 lpd (60,000 gpd) RO unit, which represents a significant scale-up compared to previous RO studies of AMD treatment, is fully capable of treating ferrous AMD discharges to produce high quality water with few operational difficulties. Automated regulation of product flow rates at preset levels functioned reliably during more than 4500 hours of operating time. Module failures were minimal (four out of 84) during the period, and were the result of cracked module casings. No abnormal deterioration of membrane performance in terms of flux decline or deterioration of ion rejection was noticed during normal operations at 50 through 90 percent unit recoveries. With proper acidification of AMD (ph 2.8-3.0), and known recovery limitations of the AMD feed based on its cited characteristics, no iron or gypsum fouling will occur. Automatic low pressure shutdown and acidified backflushing systems worked well. In short, the RO unit met all design and operating specifications. The only major problem encountered was erosion/corrosion of the stub tubes connected at 90^{o} angles to the inner surface epoxy-coated pressure vessels. This resulted in pin-hole leaks in the stub tubes themselves. Welding and epoxy recoating of the defects was only a short-term maintenance measure, and the pressure vessels may eventually have to be replaced.

- Lime neutrolosis proved to be both technically and operationally unfeasible, primarily due to excessive $CaSO_4$ concentrations in the neutralized supernatant recycled to the RO unit. Several case studies and experiments demonstrated that when compared to once-through RO recovery operations on an AMD with specified chemical characteristics, lime neutrolosis is not competitive when examined from either an operational or economic perspective.

- Soda ash neutrolosis appeared to be a feasible process, if care was taken to raise pH levels to greater than 9.5 to remove calcium hardness. The economics of the process are questionable for Crown AMD, with chemical costs running in excess of 53 cents per 1000 liters ($2.00 per 1000 gallons) of AMD treated.

- Lime-soda ash neutrolosis was also an operationally viable treatment method. Costs were reduced since lime may be used to elevate the RO brine to pH 8.0 before using soda ash softening to raise pH levels to 9.5-10.0, which removes better than 90 percent of the calcium. Cost estimates of chemicals show that it would require approximately 40 cents per 1000 liters ($1.50 per 1000 gallons) to treat Crown AMD, and there exists the expense of maintaining accurate pH control in both the lime and soda ash additive steps of the process.

- In both the soda ash and lime-soda ash neutrolosis processes, there was a problem of Na_2SO_4 concentration build-up in the supernatant during the run periods. Even for the small amounts of recycle conducted in the studies, the increases in the RO brine osmotic pressures due to this effect were large. The net result to maintain a pre-set product flow under these conditions must be to increase feed pressure, and hence operating costs, at a possible sacrifice of overall product quality.

- The coupled sodium cycle CIX/RO process showed an excellent capability to function as a high recovery AMD treatment system without membrane fouling. The Na_2SO_4 laden waste brine from the process was utilized to provide up to 40 percent of the regenerating capacity of the resin bed, thus reducing NaCl requirements in regeneration. Again, with such a high recovery (greater than 90 percent) mode of operation, substantial osmotic pressures existed within the RO system, tending to reduce product flux which must be compensated for by increased feed pressure on the RO system. Product water quality from the coupled system met potable water standards except for low pH, which could be easily buffered to a 7.0 pH value.

SECTION 3

RECOMMENDATIONS

Based on the results and conclusions of the investigations, the following recommendations are made for additional studies related to RO-based and coupled CIX/RO treatment of AMD:

- The economics of once-through RO treatment of AMD should be fully investigated to include capital, operating, and maintenance costs for a complete treatment system including the RO unit, and all peripheral unit processes and hardware, with special emphasis on waste brine disposal costs.

- The cost-effectiveness of soda ash and lime-soda ash neutrolosis should be determined to establish whether they are viable processes for treatment of AMD, and indeed to find out what advantages they have, if any, over a once-through maximum recovery type RO operation.

- A counter-current CIX system coupled with RO should be studied, since there is reason to believe that even higher system recoveries can be attained owing to reduced hardness leakage from the ion exchange side of the system. Also, more detailed investigations should be made to optimize regenerant utilization when the $NaCl$-Na_2SO_4 tandem regeneration procedure is utilized. In this respect, the goal would be to minimize $NaCl$ consumption, and maximize Na_2SO_4 usage. The addition of a chemical antiprecipitant agent to the Na_2SO_4 regenerant aid should be investigated to inhibit the onset of $CaSO_4$ precipitation.

- A detailed study of the process economics of a coupled IX/RO treatment system should be performed, and a comparative cost analysis made with other types of RO based treatment techniques.

- A Manual of Practice pertinent to treatment of AMD by RO techniques should be prepared to serve as a practical AMD treatment guide to design and operating personnel in the field. There appears to be sufficient information developed to date to produce such a document.

SECTION 4

BACKGROUND

A brief presentation is made of selected benchmark studies in the areas of AMD treatment by both RO and IX systems, and IX as a pretreatment process, to provide some background for the work reported in Sections 5 through 8.

ACID MINE DRAINAGE TREATMENT BY REVERSE OSMOSIS

In late 1965, the Office of Saline Water and the Bureau of Mines supported research studies to determine the feasibility of utilizing RO to recover a potable water product from AMD (1). The tests were conducted on a continuous basis at Kittanning, Pennsylvania for a period of 10 days by the General Atomic Division of General Dynamics Corporation. Based on these short-term tests, it was concluded that the RO process was effective in concentrating and reclaiming acid minewaters. During the operation, recovery rates were maintained at more than 90 percent, and approximately 4160 lpd (1100 gpd) of high quality water was produced from a feed with a pH $\leq$ 3.0 containing 100 milligrams per liter (mg/l) or more of dissolved iron.

As a result of these early successes, two series of 13-week tests were carried out at Norton, West Virginia in 1968 (2). These studies were conducted with a 37,800 lpd (10,000 gpd) RO water treatment system that utilized high-selectivity cellulose acetate membranes in a spiral-wound configuration. The test waters had pH values ranging from 2.7 to 3.0 and contained 79 to 150 mg/l of dissolved iron (almost totally in the ferric state), depending on climatic conditions. The total dissolved solids (TDS) content in the feedwater varied from about 800 to 1,600 mg/l. To investigate any problems that might be encountered in achieving higher recovery operations, several operations at increasing levels of recovery were conducted during the first 13-week test period using 144 modules, each containing 1.02 m^2 (11 ft^2) of active membrane surface. It was determined that the system could operate for short periods at a nominal 75-percent recovery and achieve an overall salt rejection of 98 to 99 percent without any apparent iron or sulfate scaling problems.

From September 1968 to December 1968, the second 13-week test was carried out using modules having 4.65 m^2 (50 ft^2) of active membrane surface. A 957-hour experiment was conducted at a pressure of 4,137 kilonewtons per square meter (kN/m^2) [600 pounds force per square inch (600 psi)]*, and 70 percent water recovery was achieved. After this run, another experiment of 693.7 hours duration was performed at a pressure of 5,516 kN/m^2 (800 psi), and during this period the recovery was maintained between 73 and 80 percent. The work to this point thus had revealed that RO could successfully treat AMD on a relatively long-term basis at up to 75-percent recovery levels.

In 1969, further studies (3) were performed at the Norton site both to obtain additional information at 75-percent recovery for both 4,137 kN/m^2 (600 psi) and 5,516 kN/m^2 (800 psi) runs, and to investigate RO operating performance at recoveries higher than 75 percent. High-flux modules were compared with the high-selectivity modules that had been utilized in prior tests. The results illustrated that either high-selectivity modules or high-flux modules were capable of sustaining good performance for 75 percent recovery AMD treatment operations at both pressure levels. In addition, short period operation at feedwater recoveries up to 92 percent was achieved without great difficulty. It was also concluded that the high-flux modules could produce good quality product water at a flux rate one-third greater than that of the high-selectivity modules, while the rejections for both high-flux and high-selectivity modules were almost equal.

During the same period, Rex Chainbelt, Inc. (4) performed a 35-day test at Shickshinny, Pennsylvania, using a 37,800 lpd (10,000 gpd) demonstration unit to treat AMD taken from a Mocanaqua discharge. The results again indicated that the RO process had potential application in AMD treatment, and could produce a water containing about 50 mg/l TDS and 3 mg/l iron for the AMD treated in this study. Although the water composition of the Mocanaqua discharge was similar to that of the Norton water except for the ionic state of the iron (Fe^{+3} at Norton, Fe^{+2} at Mocanaqua), an iron fouling problem was encountered during the tests. It was reported, however, that a 5-percent solution of $Na_2S_2O_4$ (sodium hydrosulfite) could effectively remove the iron precipitate from the membranes; and if the iron fouling problem could be minimized, 80-percent recovery could be obtained.

Since it was implied in the previous study that a ferrous iron water was more problematic to treat than a comparable ferric iron water, it seemed prudent to make more thorough investigations on ferrous iron waters. Therefore in 1970, Morgantown, West Virginia and Ebensburg, Pennsylvania were selected by EPA as two additional test sites to study RO treatment of predominantly ferrous iron waters (5). A 15,100 lpd (4,000 gpd) spiral-wound membrane module RO unit was utilized at both locations. At the Morgantown site, the AMD feedwater had such heavy mineral concentrations that severe fouling was observed even at 50-percent recovery, and RO demineralization did not seem feasible. The experimental results obtained at Ebensburg, however, demonstrated the ability to operate an RO system on predominantly ferrous iron AMD without iron fouling by adjusting the feedwater pH; and the quality of the product water produced at Ebensburg would have been suitable for domestic or industrial purposes with some pH adjustment and filtering.

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[*] 1 psi = 6.895 kN/m^2

Although results obtained from the tests at Norton, West Virginia (1968-1969) indicated that RO could recover up to 75-percent product water (permeate)* from AMD, a continuing, identifiable process problem was the disposal of the waste brine (concentrate)*. Treatment of AMD by a combination of neutralization and RO processes was thus suggested and conducted. This process consisted of operating the RO unit at its maximum recovery for raw AMD feed, with the waste brine subsequently lime neutralized, and supernatant from the neutralized brine settling tank recycled to the feedwater of the RO unit to produce a very high overall systems recovery. Hill, et al. (6), concluded that this RO/neutralization (neutrolosis) process could obtain 98-percent water recovery based on raw feed flow when applied to a high ferric to ferrous iron AMD, and generate sludge suitable for disposal through permanent landfill. The major unknowns to be resolved in the neutrolosis treatment of AMD were whether it could be successfully operated on ferrous iron AMD, whether it could sustain long-term operations without significant $CaSO_4$ fouling, and whether there would be any effects of the process on membrane life and performance.

Through a grant to the Commonwealth of Pennsylvania in 1971, EPA contracted with Rex Chainbelt, Inc., to further evaluate the iron fouling observed in the 1969 Mocanaqua studies (7). Three types of RO membrane systems, i.e. tubular, spiral-wound, and hollow-fiber were utilized during these investigations. The results indicated that membrane fouling due to iron was controlled by adjusting feed pH to 2.8 with acid injection, but the recovery of product was limited to about 75 percent due to calcium sulfate fouling. The study also showed, in one typical case, that a product water containing 25 mg/l TDS could be produced from an AMD containing 1319 ppm TDS, and that the average rejection of individual ions across the RO membrane was in the range of 99.2 to 99.7 percent. In addition, it was concluded that the performance of spiral-wound RO membrane systems was superior to that of the tubular and hollow fiber concepts.

Based on the success of previous investigators to utilize RO to produce nearly potable water from AMD and simultaneously minimize iron fouling problems, EPA decided to initiate pilot plant scale studies to further examine the applicability of using RO-based processes to treat AMD. In 1971, work was started to install a 227,000 lpd (60,000 gpd) spiral-wound RO membrane system demonstration plant at the Crown Mine Drainage Control Field Site, Rivesville, West Virginia,to provide data on RO systems scale-up and its ability to sustain long-term operations. Also to be studied was the feasibility and reliability of neutrolosis as a high recovery/low waste treatment process for ferrous iron type AMD. In 1973, a 240-hour continuous shakedown run was conducted at Crown using the 227,000 lpd RO unit operating at 50-percent recovery on a once-through basis. Blackshaw, et al., (8), concluded that the RO unit did demonstrate the capability of successfully treating Crown AMD at this recovery level without membrane fouling or major operational difficulties.

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*Readers familiar with RO technology may be more accustomed to using the terms permeate and concentrate to denote product (or product water) and waste brine, respectively.

ACID MINE DRAINAGE TREATMENT BY ION EXCHANGE

Ion exchange (IX) has been widely used for many years to produce limited quantities of potable water from brackish water, but its application to AMD treatment is relatively recent. In 1967, Pollio and Kunin (9), reporting the results of laboratory studies conducted by Rohm and Haas Co., concluded that an Amberlite IRA-68 ion exchanger operating in the bicarbonate cycle could be used to yield a water of quality suitable for industrial, agricultural, and domestic uses from a 3,000 mg/l (as $CaCO_3$) sulfates synthetic AMD. The ion exchange reactions for valence + 2 cations were described as follows:

$$\begin{array}{llcllcll}
\text{Service:} & M(SO_4) & + & R^a(HCO_3)_2 & \rightarrow & R^aSO_4 & + & M(HCO_3)_2 \\
\text{Regeneration:} & R^aSO_4 & + & 2NH_4OH & \rightarrow & R^a(OH)_2 & + & (NH_4)_2\,SO_4 \\
 & R^a(OH)_2 & + & 2H_2CO_3 & \rightarrow & R^a(HCO_3)_2 & + & 2H_2O
\end{array}$$

In this process, most of the metal (M) sulfates contained in the AMD were converted to soluble bicarbonates (HCO_3) which passed through the anion resin (R^a) bed without forming precipitates. The effluent from the ion exchanger was further treated by aeration, lime-softening, and subsequent clarification to yield a water of useful quality. The regenerants used in this process were ammonia and carbon dioxide. Estimates showed that the total cost to process an AMD water was within the range of 25 to 50 cents per 1,000 gallons, depending on regenerant costs, the quality of product water desired, and the anion content of the acid mine waters. It was also suggested that for economic treatment of AMD by the Amberlite IRA-68 ion exchanger, the anion contents of acid mine waters should be limited to less than 4,000 mg/l as $CaCO_3$.

In 1971, Kunin and Downing (10) discussed the performance of a Desal® process which was also developed by Rohm and Haas Co.. Besides a basic weak-base anion exchange resin, using either Amberlite IRA-68 or IRA-93, the Desal® system included a cation exchanger for the additional removal of cations from acid mine water. The exhausted cation exchange resin was regenerated with acid; and in this treatment of AMD, the metal concentration of feedwater was reduced tenfold from 3,000 mg/l to 300 mg/l.

Another IX process for treatment of acid mine waters, developed by Nalco Chemical Corp., was known as the Sul-biSul® process (11, 12). The Sul-biSul® process utilized a strong acid cation exchange (CIX) resin and a strong-base anion exchange resin which operated in the sulfate-bisulfate cycle. As in conventional deionization, the water to be treated was first contacted with a strong acid exchange resin. The effluent from this resin containing essentially sulfuric acid was then passed through a strong anion exchanger in the sulfate form to subsequently remove the anions (especially sulfate ions) contained in the solution. Thus the ADM was effectively demineralized. The service cycle reactions were:

Cation Exchanger: $MSO_4 \quad + \quad 2R^cH \quad \rightarrow \quad R^{c2}M \quad + \quad H_2SO_4$

Anion Exchanger: $H_2SO_4 \quad + \quad R^aSO_4 \quad \rightarrow \quad R^a(HSO_4)_2$

where R^c denotes the cation exchange resin.

The regenerant for the exhausted cation exchange resin was sulfuric acid, while the anion resin was simply regenerated by water, or water slightly alkaline with lime.

Care and Zawadzki (13) had also conducted studies on AMD treatment in 1965 by using only a strong-base anion resin in the sulfate form. They found that for every unit of AMD treated, three units of water were needed to regenerate the resin, and the liberated acid was rather dilute because of this high ratio of regenerant to feed. Cost of treating 3,785,000 lpd (1,000,000 gpd) at that time was estimated at 8 cents per 1,000 liters (30 cents per 1,000 gallons).

In 1964, Nalco Chemical Corp. had run pilot plant studies at the Smith Township plant (a municipal water plant) in Washington County, Pennsylvania, using fixed IX beds consisting of one anion exchanger and one cation exchanger. Based on the promising results obtained from this pilot plant, a semi-commercial IX treatment plant was constructed and full-scale treatment was initiated in late January 1971 (11). A typical analysis of the raw water at Smith Township indicated a pH of 6.5 to 8.4, TDS of 1,500 to 2,000 mg/l, and total hardness as $CaCO_3$ ranging from 590 to 1,800 mg/l. Prior to the installation of the IX treatment plant, this water had been treated by coagulation and lime softening followed by filtration and chlorination. This treated water had a pH range of 8.5 to 8.7, 1,500 mg/l total dissolved solids, and 450 to 600 mg/l total hardness. After 1971, a product water with a pH value between 8 and 9, TDS concentration of less than 500 mg/l, and a total hardness of 150 mg/l was obtained from the Smith Township IX treatment plan in which two Chem-Seps continuous IX units were installed.

In 1973, Kunin and Demchalk (14), reporting on work done at the Hawk Run AMD treatment plant, indicated that the modified Desal® process was an effective method for treating AMD water. In the modified Desal® process, a weak-base anion exchange resin exchanged bicarbonate ions for sulfate ions in the acid mine water. In addition to removing the sulfates, this process also converted the metal sulfates into soluble metal bicarbonates with the subsequent removal of calcium, magnesium, iron, manganese, and aluminum by degasification, aeration, and softening. The product water obtained had good quality and met drinking water standards established by the USPHS.

The Culligan International Company also made an extensive study (for EPA) of the treatment of AMD by IX. In 1972 Holmes and Schmidt (15) reported on the applicability of five selected IX resin systems to treat AMD. The five resin systems studied were:

1. a strong-acid cation exchanger regenerated with sulfuric acid.
2. a strong-acid cation exchanger regenerated with sodium chloride.
3. a weak-base anion exchanger regenerated with caustic soda.
4. a weak-base anion exchanger regenerated with sodium hydroxide and carbon dioxide (modified Desal® process).
5. a strong-base anion exchanger operated like the Sul-biSul® process.

A specific process employing a strong-acid cation exchanger (hydrogen form), followed by a weak-base anion exchanger (free-base form), with post treatment consisting of pH elevation to 9.9, aeration, filtration, and final pH correction was found successful. Liquid wastes from this process were acidic and required subsequent treatment and disposal. The chemical costs for producing water by this process were estimated then at 22 cents per 1000 liters (83 cents per 1,000 gallons) when applied to a synthetic AMD of the following composition:

Free Mineral Acidity (FMA), mg/l $CaCO_3$	500
Sulfate, mg/l SO_4	1150
Calcium, mg/l Ca	200
Magnesium, mg/l Mg	24
Aluminum, mg/l Al	15
Manganese, mg/l Mn	8
Total Iron, mg/l Fe	210

A second process also found to work well used a weak-base anion exchanger (Rohm and Haas IRA-68) in the bicarbonate form followed by aeration, lime treatment, filtration, and final pH correction. The chemical costs for producing water by this process were virtually identical to the above treatment method when applied to the same synthetic AMD solution. The wastes from this process were an alkaline liquid and a lime-treated sludge.

In addition, it was concluded that a strong-acid cation exchanger in the sodium form offered less potential for the direct production of potable water than the hydrogen form, since sodium ions merely had been substituted for divalent and trivalent cations.

EFFECT OF ION EXCHANGE PRETREATMENT ON OTHER PROCESSES

In 1961, programs to test the effect of IX pretreatment to enhance the water yield from desalting processes were sponsored by the Office of Saline Water. McIlhenny (16) in 1962 reported the results of a program of first softening seawater by CIX before feeding to a seawater evaporator. The pilot plant utilized for these tests was designed and constructed by the Texas Division of the Dow Chemical Company and supported by the Office of Saline Water. From this experiment, it was found that seawater could be softened sufficiently by Dowex 50W CIX resin so that $CaSO_4$ precipitation was prevented when the softened seawater was evaporated to a concentration of four times that of normal seawater. Apparently the evaporator blowdown could also have been used to regenerate the IX resin with no additional regenerant required. Estimates in 1962 showed that for a plant having a product capacity of 37,850,000 lpd (10,000,000 gpd), seawater softening would cost 2.5 cents per 1000 liters (9.4 cents per 1,000 gallons) at a brine concentration whose Cl^- normality was four times that of the input seawater.

During the course of this seawater research, it was evident that similar water treatment techniques could be used to treat other saline waters. Therefore, five laboratory IX tests of a synthetic Roswell, New Mexico water and a pilot plant scale testing program on actual Roswell water were developed and conducted (16). Results showed that Dowex 50W CIX resin successfully softened both synthetic and actual Roswell well water, along with utilization of the evaporator blowdown to regenerate the spent IX resin.

In 1965, advanced large-scale research on pretreating high salinity Roswell brackish water (3,500 mg/l hardness, and 20,380 mg/l TDS as $CaCO_3$) was performed. Crits, et al., (17) indicated that the ion exchange regeneration was accomplished using a simulated 4x-evaporated blowdown, and a resin capacity was obtained of about 41.2 kilograms as $CaCO_3$ per cubic meter (kg as $CaCO_3/m^3$) [18 kilograins per cubic foot (18 kgr/ft^3)].* More recently, Kingsbury and Schomaker (18) have discussed the application of a coupled IX/RO process system to a brackish well water at Greater Pine Island, Florida. They indicated that a resin capacity of 29.8 kg $CaCO_3/m^3$ (13 kgr. $CaCO_3/ft^3$) was obtained by using the waste brine regenerant produced by a RO unit operating at 91-percent recovery.

In 1974, three different kinds of IX softening systems coupled to an RO unit were investigated by Witmer, et al., (19) on an inland brackish water. The three systems investigated were:

System (I).	Ion Exchange (weak-acid)---sulfuric acid regeneration.
System (II).	Ion Exchange (strong-acid)--waste brine regeneration.
System (III).	Ion Exchange Dual Bed (weak acid-strong acid)--sulfuric acid and waste brine regeneration.

In these studies high water recovery (>90 percent) was achieved from the coupled IX/RO process system without a membrane fouling problem. Simultaneously, it was found that calcium sulfate fouling during regeneration with high sulfate waste brine could be avoided with the aid of an antiprecipitant (sodium hexametaphosphate). It was concluded that the hardness leakage obtained from a weak acid IX resin (System I) in the range of 50 to 60 mg/l $CaCO_3$ was higher than the 20 mg/l $CaCO_3$ leakage which was obtained from both System (II) and System (III). Estimated softening costs indicated that a sodium-form strong-acid IX resin with waste brine regeneration appeared to be economically attractive. For a self-sufficient strong-acid CIX system, it was determined that the ratio of sodium to total hardness (as $CaCO_3$) in the strong-acid CIX feed should be greater than 1.3.

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*1 kgr/ft^3 = 2.29 kg/m^3 where 7 kgr = 1 lb = 0.454 kg

Based on the promising results of previous coupled IX/RO systems studies, investigations were conducted at the Crown Mine Drainage Control Field Site to determine the applicability of such coupling processes for AMD treatment. A sodium form strong acid ion exchanger was used as a softening pretreatment step prior to purification in a spiral-wound membrane 15,100 lpd (4,000 gpd) RO unit. The exhausted resin was regenerated by both NaCl solution and by a combined NaCl/Na_2SO_4-loaded waste brine from the RO unit. The specific goal of the studies was to determine the recovery potential of the coupled system, and the effect of utilizing Na_2SO_4 waste brine as a regenerant aid to NaCl for capacity restoration of the exhausted IX resins.

SECTION 5

DESCRIPTION OF THE PILOT PLANT FACILITY

The Crown Mine Drainage Control Field Site is located at the intersection of Stewarts Run and Little Indian Creek on ten acres of land at Crown, West Virginia, which is approximately 20 km. (12 miles) southwest of Morgantown, West Virginia. The mine drainage feed source, which is capable of delivering more than 567,000 liters/day (150,000 gallons/day), originates from a 156-mm (6-inch) bore hole pump situated 366 m (1200 ft) from the pilot plant location. The acid mine waters are transported to the pilot plant through a 78-mm (3-inch) polyvinylchloride (PVC) pipeline.

The 227,000-lpd (60,000-gpd or 60 K) and 15,100-lpd (4,000-gpd or 4K) RO units, and the twin-bed sodium-cycle CIX system are located in a 12.2 m x 30.5 m (40 ft x 100 ft) light gauge steel building which was erected by West Virginia University at the Crown Mine Drainage Control Field Site. This building, shown in Figure 1, is occupied jointly by West Virginia University and EPA. EPA operated RO and IX test equipment and neutralization systems, including aeration, and clarifier tanks pertinent to EPA lime/limestone neutralization treatment studies.

Research support facilities at the Crown Mine Drainage Control Field Site have also been installed by EPA. These include: two laboratory trailers for chemical analysis of water quality and process streams by wet chemistry, atomic absorption methods, and other instrument techniques; an aeration and waste stream clarifier system located outside the pilot plant building; a 19,000,000-liter (5,000,000-gallon) sludge settling pond; numerous pipelines to transfer mine drainage, product water, waste brine, and sludge to designated locations on the site; an office trailer; and warehouses for the storage of necessary supplies and equipment.

60K REVERSE OSMOSIS SYSTEM

Equipment

The 60K RO unit, which was manufactured by Gulf Environmental Systems, Inc., has been designed to nominally deliver a constant product water output of 227,000 lpd (60,000 gpd). This is basically accomplished by pneumatically operated automatic flow control valves in the feed and brine lines which, when preset to flow rates to yield 2.65 lps (42 gpm) product flow, will work in conjunction to adjust system operating pressures to maintain constant product output and recovery. The feed stream volume flow rate may vary from 6.56 to 2.90 lps (104 to 46 gpm), which corresponds to designed

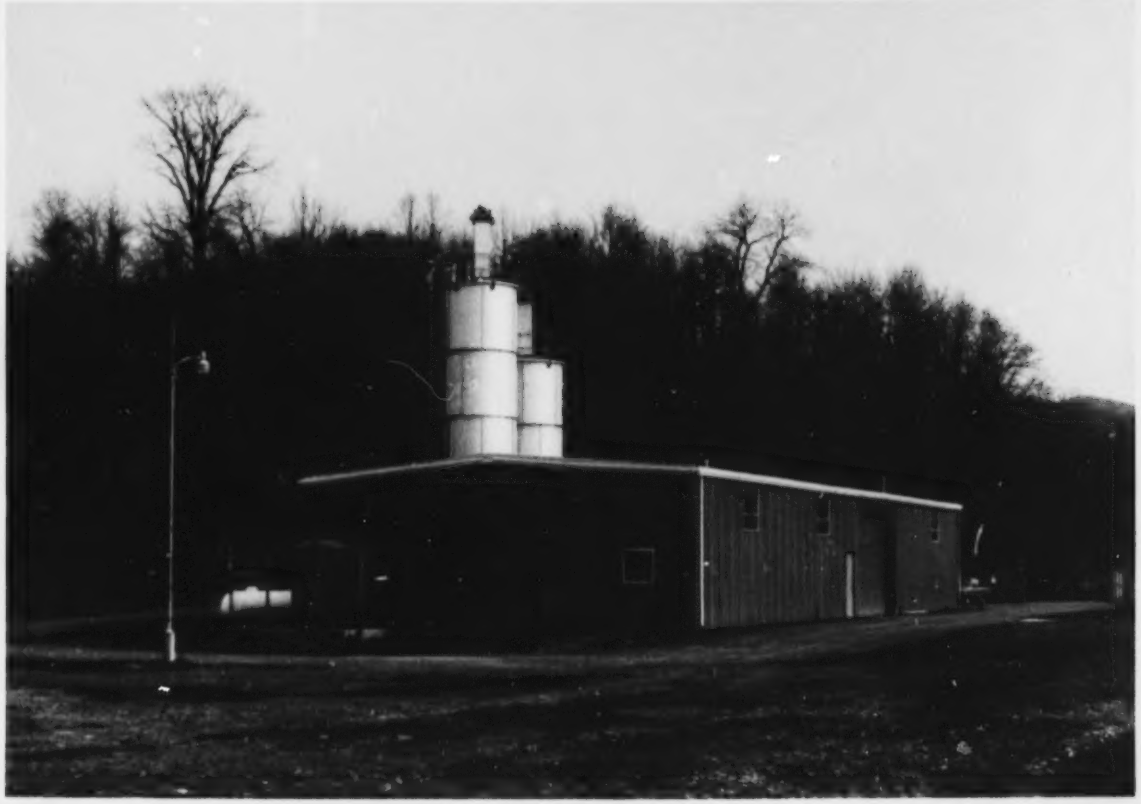

Figure 1. AMD pilot plant facility building - Crown, WV.

operational recoveries ranging from 40 percent to 90 percent. The system is composed of four major assemblies:

1. Pretreatment, product storage, and blending assembly.
2. Membrane-module pressure vessels and high pressure pump assembly.
3. Sampling and pressure measurement assembly.
4. Instrument console.

Pretreatment, **Product Storage, and Blending Assembly.**

This includes the following major components mounted on a steel frame:

a. Two stainless steel 20-micron cartridge filter assemblies arranged in parallel to remove suspended solids from AMD feedwaters.
b. An elevated 1330-liter (350-gallon) fiberglass tank for storage of acidified product water used either for product water recycle when blended feedwaters are required, or for pressure vessel backflushing of modules when manual or automatic shutdown occurs.
c. Two chemical feed pumps and pH flow sensor assemblies to assist in maintaining pH control of feedwater and product water respectively via injection of sulfuric acid.
d. A centrifugal pump and orifice-type rotameter to maintain and measure manually controlled rates of product water recycle.
e. A liquid-level electrode in the product water storage tank to ensure a proper inventory of product water for recycle and backflushing purposes.

Membrane-Module Pressure Vessel and High Pressure Pump Assembly--

The membrane-module pressure vessel assembly is composed of fourteen pressure vessels and the appropriate interconnecting piping mounted on a steel frame. The feed and brine control valves are attached to the frame, and the two Goulds Model 45600-SS high pressure pumps are mounted on top of the pressure vessels.

The pressure vessels are nominal 102 mm (4 inch) diameter, Schedule 40 carbon steel pipe, 6.1 m (20 ft) long, and are lined with a modified phenolic coating to prevent corrosion. Each vessel is grooved on both ends for Victaulic couplings which secure the vessel end caps. These caps are composed of PVC with a stainless steel bearing ring installed on the perimeter. The end caps are threaded for attaching product water lines from the vessels to the sampling panel. The feed and brine streams enter and exit the pressure vessels from the side, and these fittings are welded into the vessel. Victaulic couplings are used to attach and connect the feed and brine manifolding.

Each pressure vessel contains six ROGA® spiral-wound cellulose acetate membrane modules of 6.5 m^2 (70 ft^2) area connected in series. The modules are joined together by couplings and centered in the pressure vessel by PVC centering devices. A chevron rubber seal, which is actuated by differential pressure, is attached to the upstream end of each module surrounding its perimeter. This seal forces the feedwater to flow through the module and exposes it to the membrane surface.

The feedwater from the pretreatment assembly is introduced to the suction side of the Goulds pumps. After pressurizing, the feed flow is controlled by a pneumatic normally-open valve, flow orifice, and flow controller. The desired flow rate is determined by the recovery level at which the unit is to operate, which in turn dictates the various pressure vessel series-parallel manifolding arrangements that have been incorporated in the unit design to permit maximum flexibility in desired recovery modes of operation.

The brine (concentrate) is discharged to a drain through a 25-mm (1-inch) pipe. A 25-mm (1-inch) control valve, orifice, and controller similar to the feed control is installed in this line.

The brine control valve is supplied with two sets of trim, i.e. valve stem and seat. This is to allow the valve to exert proper control over a range of flows. Since projected brine flow rates of 3.91 to 0.25 lps (62 to 4 gpm) represent too wide a range for a single valve to control adequately, each set of valve trim has its own flow orifice with respective CV's (flow coefficients) of 5.0 and 1.2. These matching orifice plates are sized for maximum flows of 4.41 to 1.57 lps (70 and 25 gpm), respectively. The larger CV trim and orifice are used for recoveries from 40 percent up to and including 65 percent, whereas the small CV trim and orifice are utilized for recoveries ranging from 70 to 90 percent.

It should further be noted that the 38-mm (1.5-inch) feed control valve is supplied with a single set of trim (CV 5) and a single orifice plate having maximum flow of 6.94 liter/sec (110 gpm), which is adequate to cover the feed flow of 6.56 to 2.90 liter/sec (104 to 46 gpm). Also, two Goulds multistage high pressure pumps are both required up to and including 80-percent recovery. Above that, one pump is sufficient.

Sampling and Pressure Measurement Assembly--

Valves and gauges necessary to sample pressure vessel product flow, pump discharge and inlet feed pressures, pressure drops (ΔP) across pressure vessel (tube) banks, temperature, and osmotic pressure are included on a panel board assembly.

Three-way valves are utilized to direct the product from each individual pressure vessel to a common collection manifold or to a sampling port. When a product line is sampled, the total volume from that pressure vessel is diverted to the sample port. The osmotic pressure can be measured at this time. The total product flow is measured with an orifice-type rotameter installed downstream from the collection manifold.

The operating pressure and ΔP of each bank of pressure vessels are measured using an additional set of valves.

Instrument Console--

The instrumentation necessary to control and monitor the system feed and brine flow rates, pH, conductivity, and pump operation are enclosed in an instrument console. The description and function of the major components are detailed below:

a. Two flow indicator controllers to preset, monitor, and control the feed and brine flow rates of the RO unit.

b. A conductivity meter with selector switch to monitor both brine and product water conductivities.

c. Two pH controller/transmitters to monitor and control set values of AMD feedwater and product water pH.

d. A liquid level controller for maintenance of desired product water inventory in the 1330-liter (350-gallon) storage tank.

e. Control relays to immediately shut off all pumps, and automatically backflush the system on a 5-to 30-minute time delay basis utilizing the gravity head of the stored acidified product water for any of the following fault conditions:

    (1) Low feed pressure to the high pressure pump(s).
    (2) High system operating pressure.
    (3) Low instrument air pressure.
    (4) High conductivity of brine (or product).

f. Appropriate electric power and pump operating switches, instrument air regulators, and electrical circuit breakers.

Process Description

Basic 60K Reverse Osmosis Treatment Process--

Acid mine feedwater from the bore hole pump (Figure 2) enters the pilot plant facility and is piped to a 9500-liter (2500-gallon) holding tank (Figure 3). Then it is transferred by a centrifugal pump to the pretreatment skid (Figure 4) where sulfuric acid is added to adjust the pH to 2.9. The feed is subsequently filtered by 20-micron cartridges to remove suspended solids prior to entering the main high pressure feed pumps.

The volume discharged from these pumps is automatically controlled by means of a differential pressure flow controller and control valve. The feed is then distributed via manifolding to the series-parallel array of fourteen pressure vessels, each containing six spiral-wound ROGA® modules. The concentrate flow is controlled similarly to the feed flow, so that once the two controllers are set, the unit will then operate at constant recovery, and the unit pressure will vary to maintain constant product flow rates. This system is shown in Figure 5.

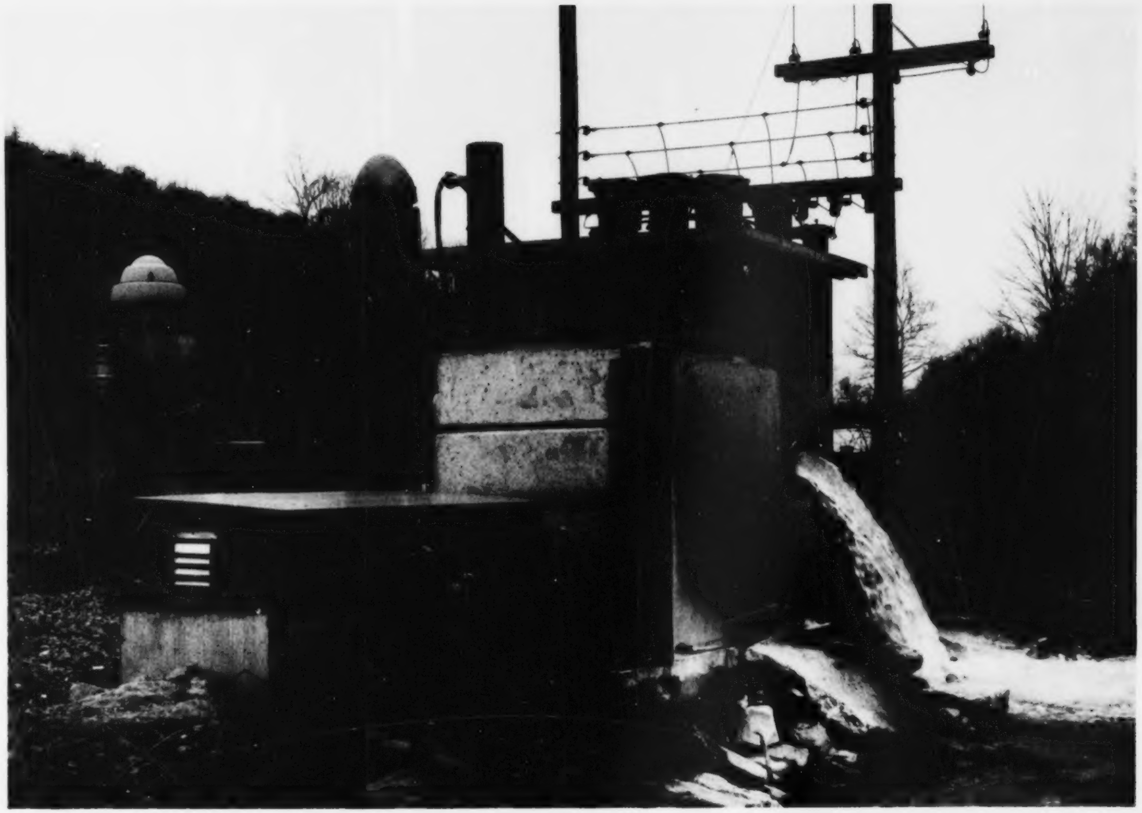

Figure 2. AMD bore hole pump - Crown, WV.

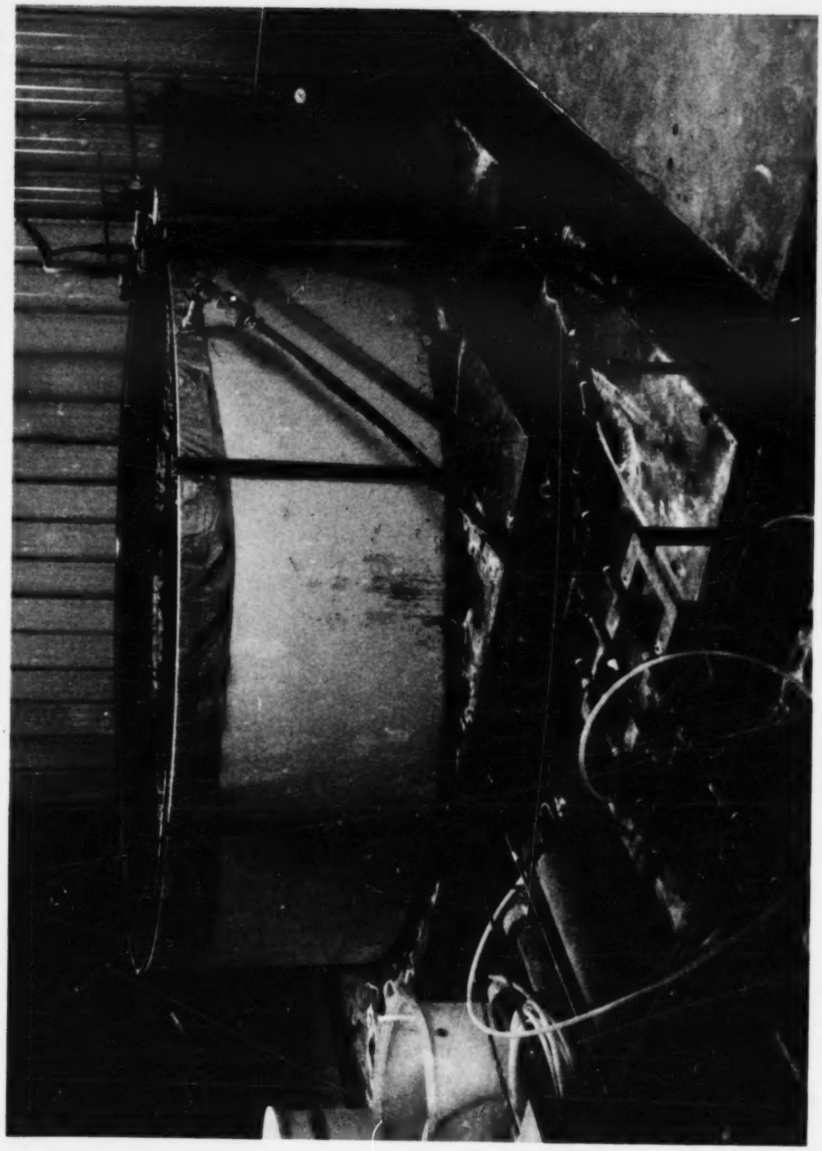

Figure 3. Main 9500-liter (2500-gallon) and AMD holding tank.

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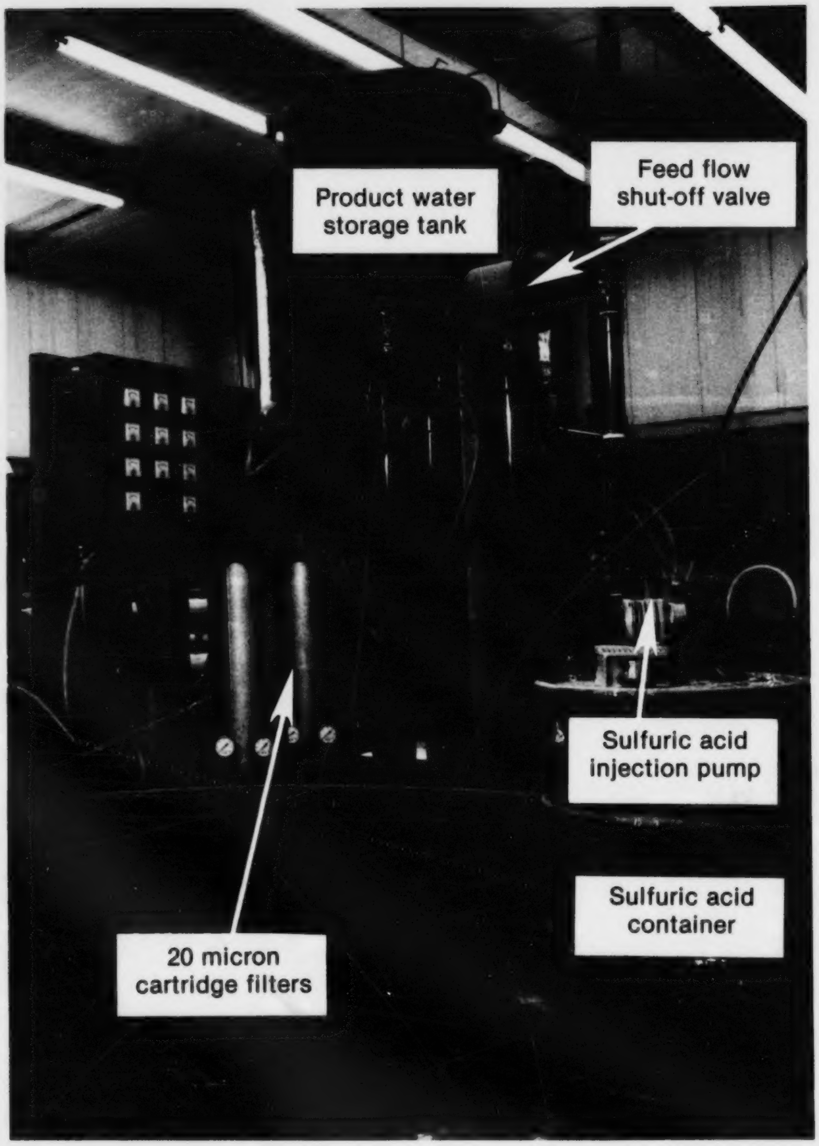
Product water storage tank
Feed flow shut-off valve
Sulfuric acid injection pump
Sulfuric acid container
20 micron cartridge filters

Figure 4. Pretreatment and product storage and blending assembly (60K RO unit).

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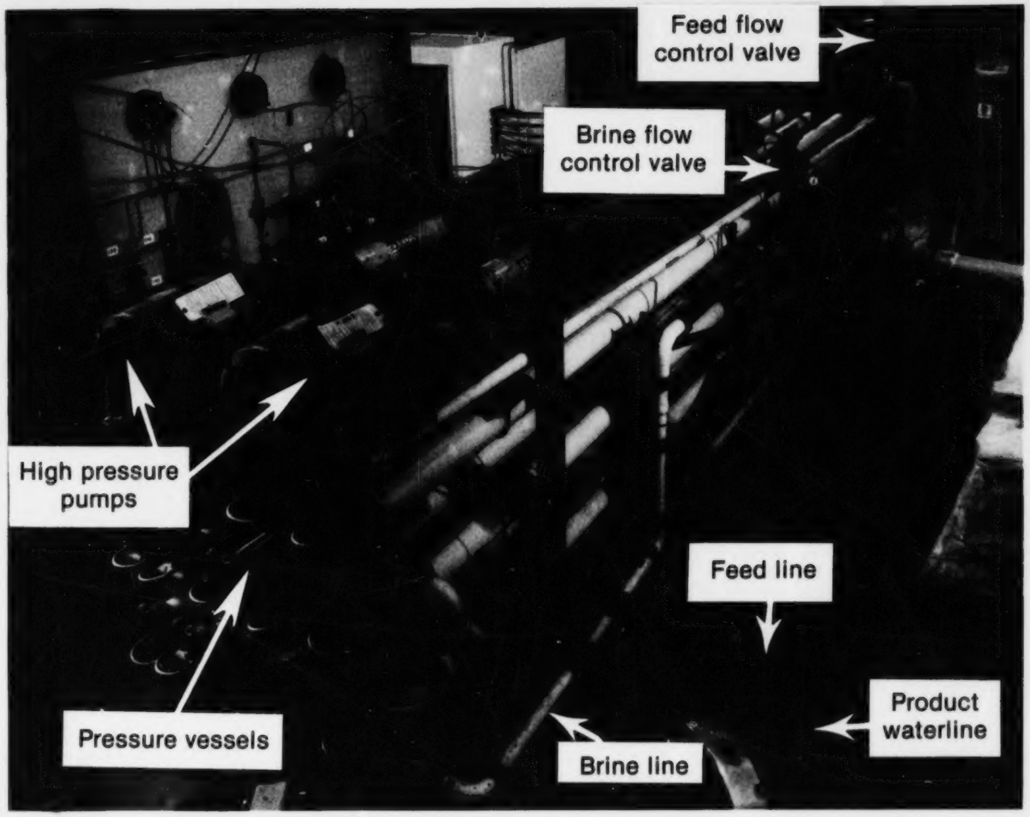
Feed flow control valve
Brine flow control valve
High pressure pumps
Feed line
Product waterline
Pressure vessels
Brine line

Figure 5. Membrane-module pressure vessels and high pressure pump assembly (60K RO unit).

The product from each pressure vessel is piped to a sampling panel where it can be measured independently (Figure 6). Provisions for measuring the osmotic pressure of each tube, as well as the pressure and ΔP of each bank of vessels are included. The product streams are collected downstream of the sampling valves and piped to the 1330-liter (350-gallon) elevated product water storage tank. The product flow is measured by means of an orifice-type rotameter and the water is pH-adjusted just prior to entering the tank. This water can then be used to dilute the feed stream at recovery levels above that where calcium sulfate precipitation is expected, or utilized for flushing the pressure vessels during unattended or scheduled shutdowns.

A centrifugal pump, manual valve, and orifice-type rotameter are used to determine the amount of product water blended with the feedwater. The flushing system includes a normally open valve and electric-pneumatic controls. The flushing sequence will begin at a preset number of minutes after shutdown. A ball valve in the line can be closed when flushing is not desired.

Product water in excess of that needed to maintain a proper inventory in the storage tank has its pH raised to a level of 6.5 before it is discharged to a floor drain outlet to Little Indian Creek. When not conducting specific neutralization or neutrolosis studies, waste brine is usually lime-neutralized in a 2300-liter (600-gallon) reactor vessel to pH levels in the 5.5 to 6.5 range (Figure 7), and then pumped to the Crown Mine Drainage Control Field Site sludge settling pond (Figures 8 and 9).

A representative process flow diagram for the initial 50-percent recovery shakedown test of the 60K RO unit is shown in Figure 10.

Manifolding Arrangements of Pressure Vessels for Different Recovery Levels--

The module pressure vessel assembly flow scheme is such that pressurized feed water is directed to a number of pressure vessels in parallel, and the concentrate from these vessels becomes the feed for the next parallel set, etc. The actual number of pressure vessels in parallel (or in a bank), and the number of these banks in series, is dependent on the operating recovery level. The reason for the parallel-series array is to maintain optimum brine velocities. As the recovery level is increased, and the product output is maintained constant, there is less brine; therefore, less vessels are in parallel and the series must then get longer.

Each of the 6.1-m (20-ft) long pressure vessels contains six spiral-wound membrane modules which nominally deliver 2725 lpd (750 gpd) of product water (at 55°F) per module. The minimum recommended brine flow is 0.25 lps (4 gpm) per module while the maximum is 0.76 lps (12 pgm) [brine/product flow rates of 8:1 and 24:1, respectively], assuming a product water output of 0.03 lps (0.5 gpm) per module. The parallel-series array configurations required for the various recovery ranges are presented in TABLE 1.

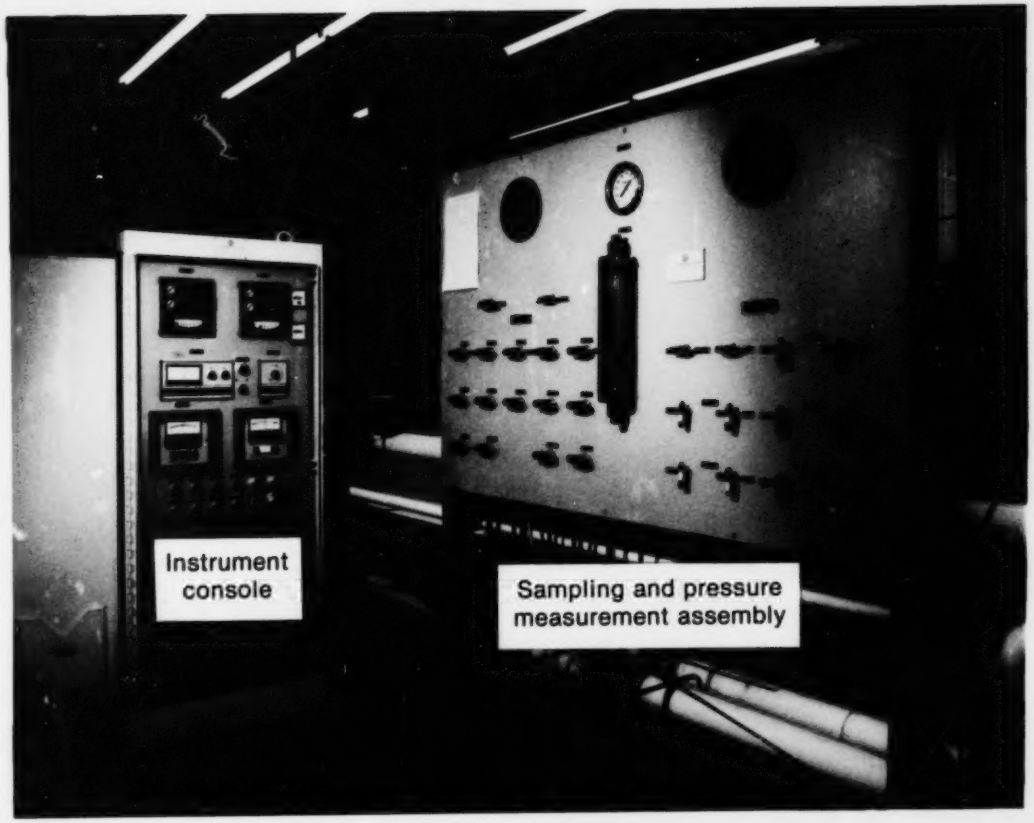
Instrument console
Sampling and pressure measurement assembly

Figure 6. Sampling and pressure measurement assembly and instrument console (60K RO unit).

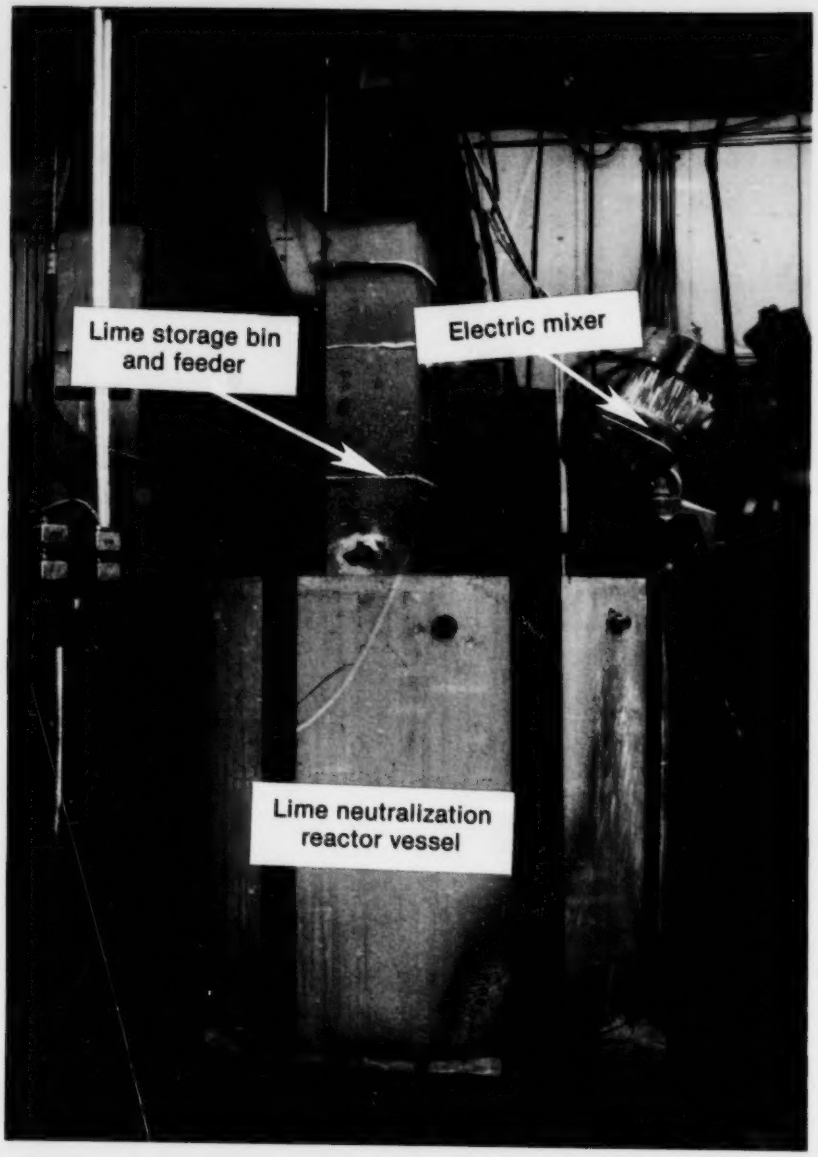
Lime storage bin and feeder
Electric mixer
Lime neutralization reactor vessel

Figure 7. RO waste brine neutralization system.

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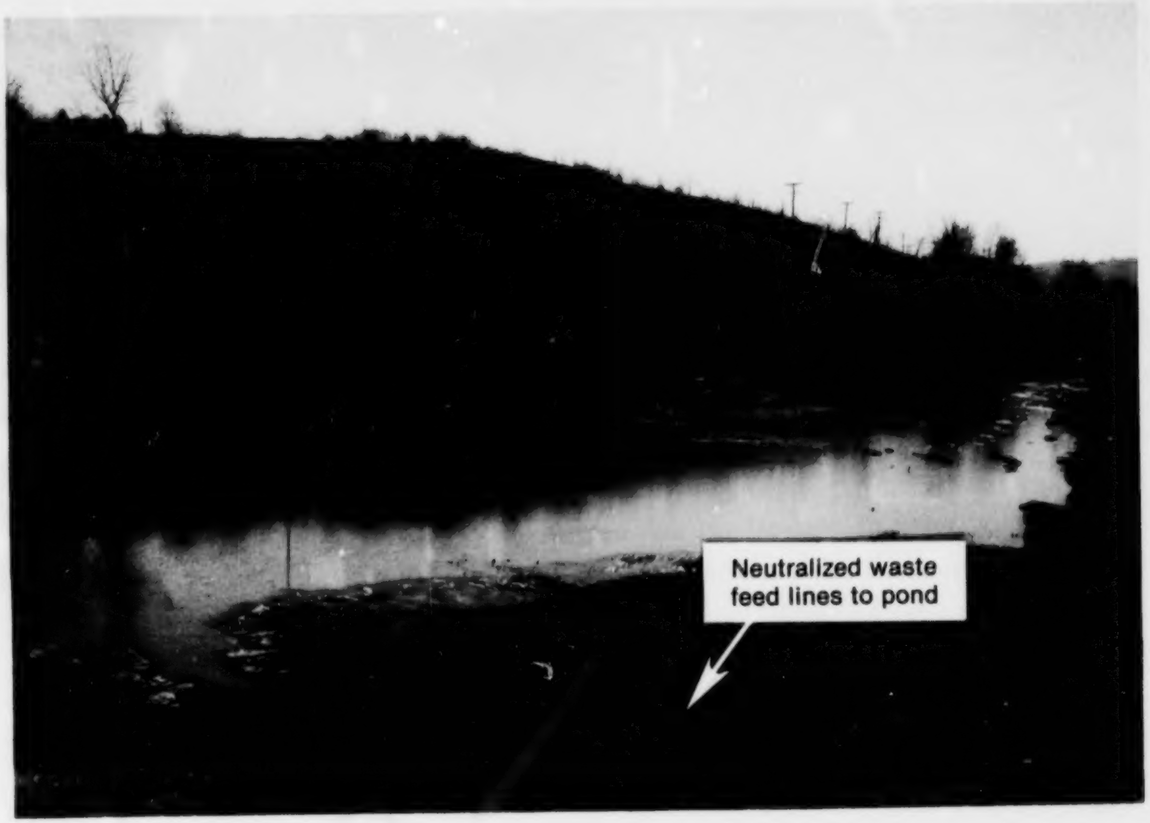
Neutralized waste feed lines to pond

Figure 8. Crown Mine Drainage Control Field Site sludge settling pond (west end view).

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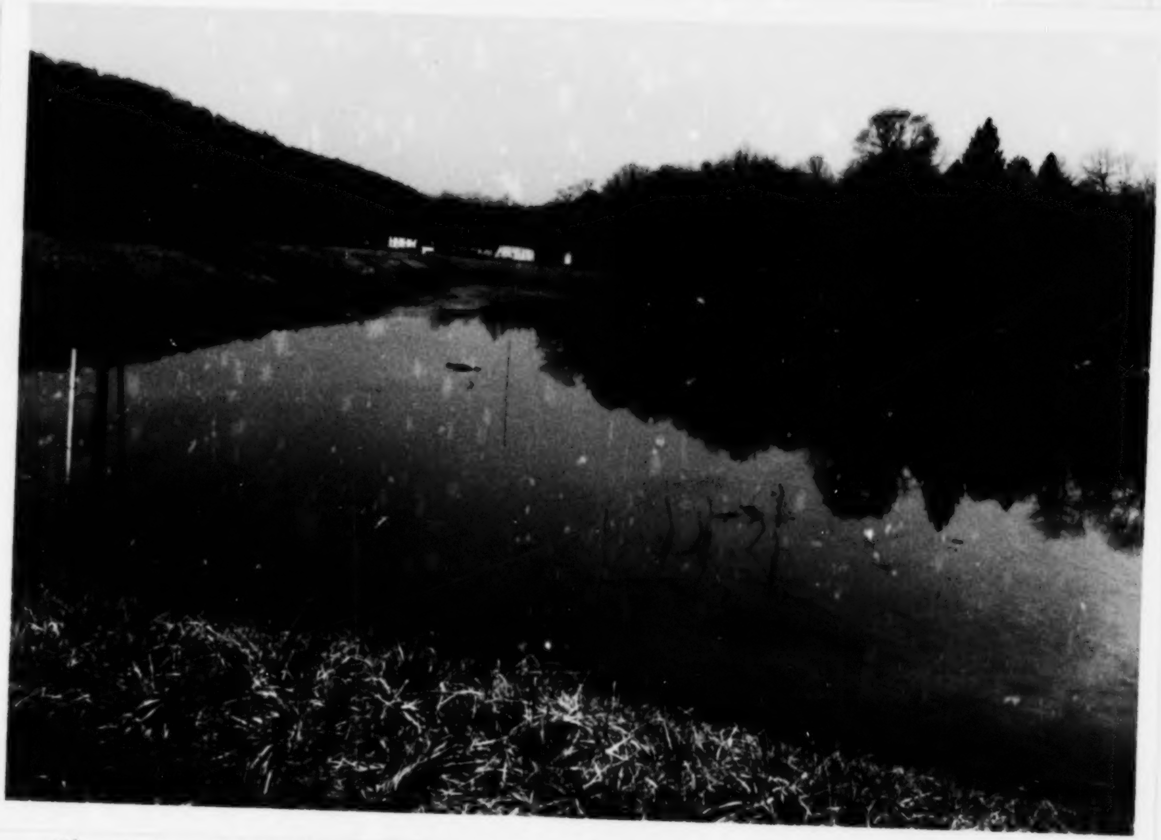

Figure 9. Crown Mine Drainage Control Field Site sludge settling pond (east end view).

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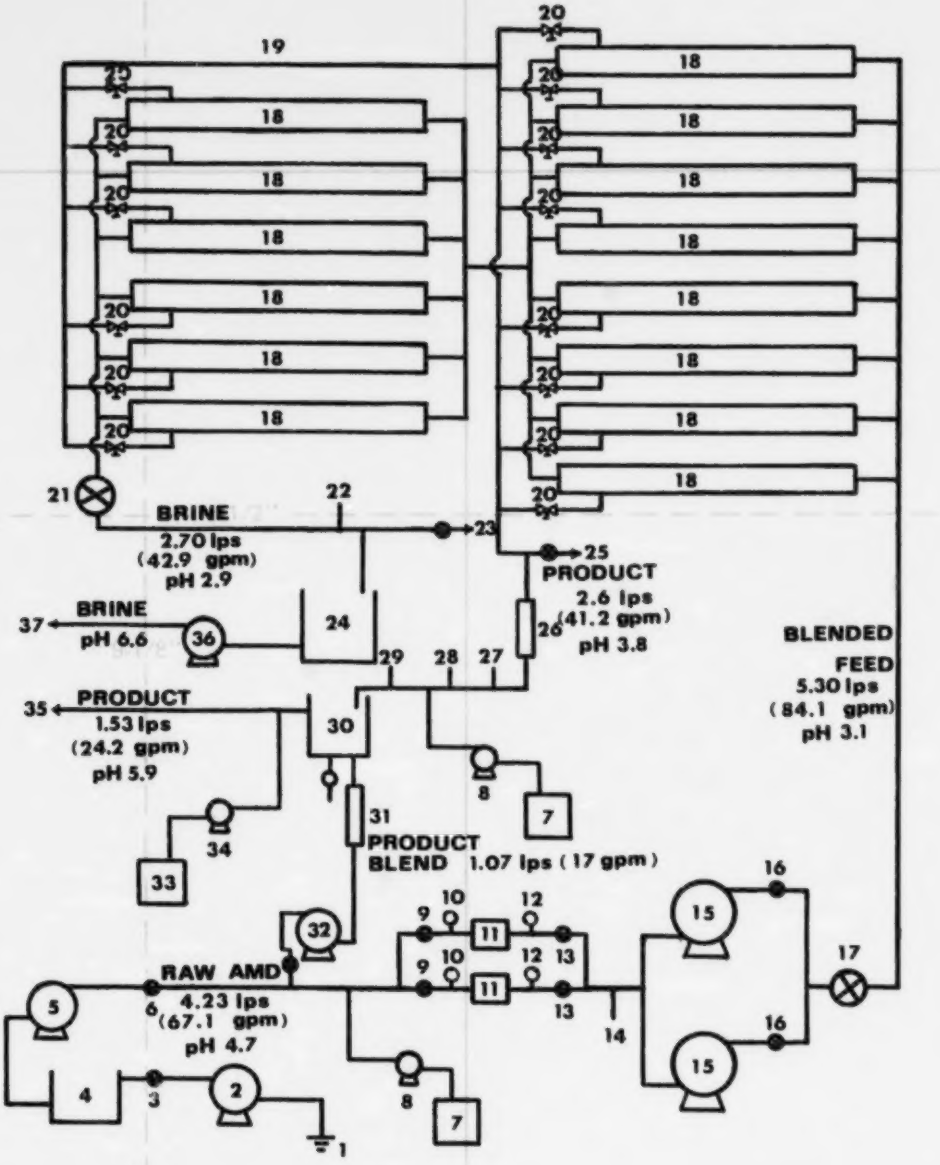
19
20
18
25
21
BRINE
2.70 lps
(42.9 gpm)
pH 2.9
22
23
25
PRODUCT
2.6 lps
(41.2 gpm)
pH 3.8
26
BLENDED
FEED
5.30 lps
(84.1 gpm)
pH 3.1
37
BRINE
pH 6.6
36
24
29
28
27
35
PRODUCT
1.53 lps
(24.2 gpm)
pH 5.9
30
8
7
31
PRODUCT
BLEND 1.07 lps (17 gpm)
34
33
16
15
17
32
RAW AMD
4.23 lps
(67.1 gpm)
pH 4.7
9
10
11
12
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Figure 10. Process flowsheet - 60K RO unit at 50-percent recovery (8-6 pressure vessel array).

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Legend for Figure 10

1. Deep Mine Bore Hole
2. AMD Transfer Pump
3. Level Control Valve
4. Raw AMD Pool
5. Feed Transfer Pump
6. Product Blend Control Valve
7. Concentrated H_2SO_4 Storage
8. H_2SO_4 Injection Pump
9. Cartridge Filter Inlet Valve
10. Filter Inlet Pressure Gauge
11. 20µ Cartridge Filter
12. Filter Outlet Pressure Gauge
13. Cartridge Filter Outlet Valve
14. Blended Feed pH Probe
15. High Pressure Pump
16. High Pressure Pump Outlet Valve
17. Feed Flow Controller
18. Pressure Vessels & RO Modules
19. Product Line
20. Product Sampling Port
21. Brine Flow Controller
22. Brine Line Conductivity Probe
23. Brine Sampling Port
24. Brine Neutralization Reactor
25. Total Product Sampling Port
26. Total Product Flow Meter
27. Product Line Conductivity Probe
28. Temperature Sensor Probe
29. Product Line pH Probe
30. Product Holding Tank
31. Product Blend Flow Meter
32. Product Blend Pump
33. NaOH Solution Tank
34. NaOH Injection Pump
35. Product to Little Indian Creek
36. Neutralized Brine Transfer Pump
37. Brine to Settling Pond

TABLE 1. 60K RO PRESSURE VESSEL CONFIGURATIONS

Array	Percent Recovery Level
8 - 6	40 - 60 %
7 - 4 - 3	60 - 75 %
5 - 4 - 3 - 2	75 - 80 %
5 - 4 - 2 - 2 - 1	85 - 90 %

TABLE 2 lists the estimated flows and brine/product ratios for each of these arrays. Note that at 60-and 75-percent recovery levels an overlapping of the usable arrays exists, while at 90-percent recovery, a low brine/product ratio occurs in the next-to-last pressure vessel. A low brine/product ratio is of concern since it results in a higher than normal solute concentration at the membrane surface, which in turn may cause fairly insoluble compounds to precipitate. These precipitated solids can foul the membrane, which inhibits system performance and ultimately results in shutdown for module cleaning and/or replacement activities.

4K REVERSE OSMOSIS SYSTEM

Equipment

The 4K RO unit, manufactured by Gulf Environmental Systems, Inc., has been designed to produce a nominal output of 15,000 liters/day (4,000 gallons/day) of high quality product water. The feed stream volume can vary from 0.44 to 0.19 lps (7 to 3 gpm), which corresponds to recoveries of 40 percent to 90 percent.

This system is also composed of four major assemblies:

1. Pretreatment assembly.
2. Membrane-module pressure vessels and high pressure pump assembly.
3. Sampling and pressure measurement assembly.
4. Instrument console.

Pretreatment Assembly--

This system includes the following major components:

a. Two PVC 10-micron cartridge filters arranged in parallel to remove suspended solids from AMD feedwaters.
b. A pH sensor in the feed line.
c. A chemical feed pump for the addition of acid to control iron precipitation.
d. An auxiliary chemical feed pump for the purpose of adding a precipitation inhibitor when desired.

TABLE 2. ESTIMATED FLOWS AND RATIOS OF BRINE TO PRODUCT FOR VARIOUS RECOVERY LEVELS -- 60K RO UNIT

Recovery (%)	Array	Bank Feed liter/sec (gpm)	Bank Product liter/sec (gpm)	Bank Brine liter/sec (gpm)	Vessel Brine liter/sec (gpm)	Brine/Product Flow Ratio
40	8	6.56 (104)	1.51 (24)	5.04 (80)	0.63 (10.0)	20.0
	6	5.04 (80)	1.13 (18)	3.91 (62)	0.65 (10.3)	20.7
45	8	5.83 (92.5)	1.51 (24)	4.32 (68.5)	0.54 (8.6)	17.1
	6	4.32 (68.5)	1.13 (18)	3.18 (50.5)	0.53 (8.4)	16.8
50	8	5.30 (84)	1.51 (24)	3.78 (60)	0.47 (7.5)	15.0
	6	3.78 (60)	1.13 (18)	2.65 (42)	0.44 (7.0)	14.0
55	8	4.79 (76)	1.51 (24)	3.28 (52)	0.41 (6.5)	13.0
	6	3.28 (52)	1.13 (18)	2.14 (34)	0.36 (5.7)	11.3
60	8	4.41 (70)	1.51 (24)	2.90 (46)	0.36 (5.7)	11.5
	6	2.90 (46)	1.13 (18)	1.76 (28)	0.29 (4.6)	9.3
60	7	4.41 (70)	1.32 (21)	3.09 (49)	0.44 (7.0)	14.0
	4	3.09 (49)	0.75 (12)	2.33 (37)	0.58 (9.2)	18.5
	3	2.33 (37)	0.56 (9)	1.76 (28)	0.59 (9.3)	18.7
65	7	4.03 (64)	1.32 (21)	2.71 (43)	0.38 (6.1)	12.3
	4	2.71 (43)	0.75 (12)	1.95 (31)	0.49 (7.8)	15.5
	3	1.95 (31)	0.56 (9)	1.38 (22)	0.46 (7.3)	14.7
70	7	3.78 (60)	1.32 (21)	2.46 (39)	0.35 (5.6)	11.1
	4	2.46 (39)	0.75 (12)	1.70 (27)	0.43 (6.8)	13.5
	3	1.70 (27)	0.56 (9)	1.13 (18)	0.37 (6.0)	12.0
75	7	3.53 (56)	1.32 (21)	2.20 (35)	0.31 (5.0)	10.0
	4	2.20 (35)	0.75 (12)	1.45 (23)	0.36 (5.8)	11.5
	3	1.45 (23)	0.56 (9)	0.88 (14)	0.29 (4.7)	9.3

(continued)

TABLE 2 (continued)

Recovery (%)	Array	Bank Feed liter/sec (gpm)	Bank Product liter/sec (gpm)	Bank Brine liter/sec (gpm)	Vessel Brine liter/sec (gpm)	Brine/Product Flow Ratio
75	5	3.53 (56)	0.94 (15)	2.58 (41)	0.51 (8.2)	16.4
	4	2.58 (41)	0.75 (12)	1.83 (29)	0.45 (7.2)	14.5
	3	1.83 (29)	0.56 (9)	1.26 (20)	0.42 (6.7)	13.3
	2	1.26 (20)	0.38 (6)	0.88 (14)	0.44 (7.0)	14.0
80	5	3.28 (52)	0.94 (15)	2.33 (37)	0.47 (7.4)	14.8
	4	2.33 (37)	0.75 (12)	1.57 (25)	0.39 (6.2)	13.5
	3	1.57 (25)	0.56 (9)	1.00 (16)	0.33 (5.3)	10.7
	2	1.00 (16)	0.38 (6)	0.63 (10)	0.31 (5.0)	10.0
85	5	3.09 (49)	0.94 (15)	2.14 (34)	0.43 (6.8)	13.6
	4	2.14 (34)	0.75 (12)	1.38 (22)	0.34 (5.5)	11.0
	2	1.38 (22)	0.38 (6)	1.00 (16)	0.50 (8.0)	16.0
	2	1.00 (16)	0.38 (6)	0.63 (10)	0.31 (5.0)	10.0
	1	0.63 (10)	0.19 (3)	0.44 (7)	0.44 (7.0)	14.0
90	5	2.90 (46)	0.94 (15)	1.95 (31)	0.39 (6.2)	12.4
	4	1.95 (31)	0.75 (12)	1.19 (19)	0.30 (4.8)	9.5
	2	1.19 (19)	0.38 (6)	0.82 (13)	0.41 (6.5)	13.0
	2	0.82 (13)	0.38 (6)	0.44 (7)	0.22 (3.5)	7.0
	1	0.44 (7)	0.19 (3)	0.25 (4)	0.25 (4.0)	8.0

Membrane-Module Pressure Vessels and High Pressure Pump Assembly--

The central assembly of the RO unit consists of three pressure vessels and related piping mounted on a steel frame. One Goulds MB 13600 SS-ceramic multi-stage centrifugal pump is mounted on the base of the unit assembly.

The pressure vessels are nominal 102 mm (4 inch), Schedule 40 carbon steel pipes, 3 m (10 ft) long, and lined with a corrosion resistant phenolic coating. The construction details of these vessels are similar to those of the 60K unit pressure vessels. Each vessel contains three spiral-wound modules, each 0.9 m (3 ft) in length, 95.3 mm (3.75 inch) in diameter, consisting of 4.65 m^2 (50 ft^2) of modified cellulose acetate membrane. The three modules are connected in series.

The three pressure vessels are arranged in a 2 - 1 array in order to maintain the optimal product/brine flow ratio in each vessel. The first two vessels are in parallel, with the brine concentrate from these vessels combining to serve as the feed to the third vessel. Figure 11 is a photograph of the 4K RO system.

Sampling and Pressure Measurement Assembly--

Three-way valves are utilized to direct the product from each individual pressure vessel to a collection manifold which channels the product to a single sample line. When the product output from a pressure vessel is sampled, the entire output of that vessel is diverted. This permits the measurement of the output of a vessel and allows chemical analyses to be performed on the product of each vessel.

A separate pressure gauge is provided to continuously monitor the feed pressure. A system of pressure taps is connected to a second pressure gauge for the measurement of the pressure drop across each pressure vessel. Necessary valve arrangements are provided to allow the pressure drop measurements to be made with one gauge. This gauge can also be used to determine the osmotic pressure difference between the product stream and brine (concentrate) stream of each pressure vessel. With the pressure tap manifold set to measure the pressure drop through the membrane, and the product flow shut off, the resulting pressure difference shown on the gauge is the osmotic pressure difference between the product and brine.

Instrument Console--

The following components are provided on the console:

a. A pressure gauge to monitor the feed pressure and a manual valve to regulate the pump by-pass, which controls the feed pressure.

b. A pressure gauge and associated pressure taps to permit the measurement of pressure drops across each pressure vessel, and the osmotic pressure, as noted previously.

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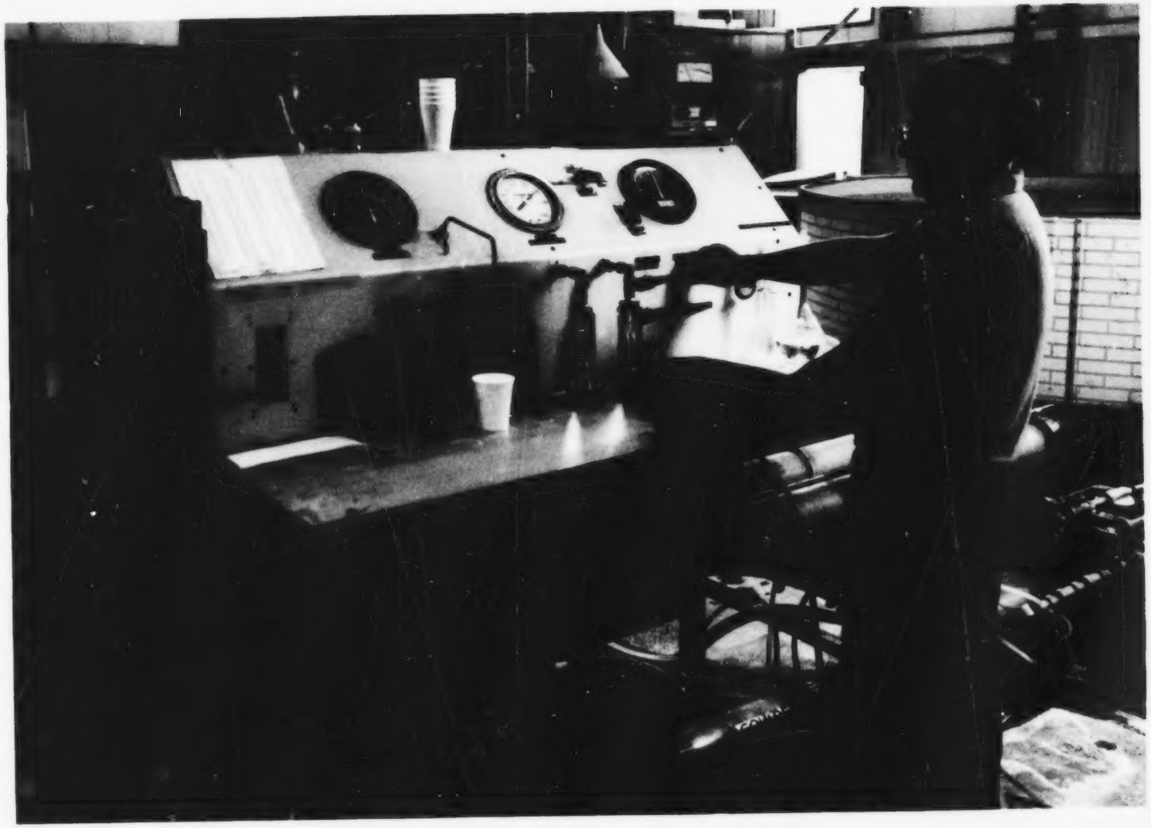

Figure 11. Membrane-module pressure vessels, sampling and pressure measurement assembly, and instrument console (4K RO unit).

c. Two rotameters, one to measure the raw feed flowrate, and one to measure the total product water output.

d. One temperature gauge for monitoring the temperature of the feed water.

e. A pH meter to monitor the feed pH because of the necessity for maintaining rather stringent control over the pH.

f. A brine recycle valve which adjusts the amount of brine recycled, and thus provides control over the unit product recovery.

Process Description

AMD feedwater is withdrawn from the same 9500-l (2500-gal) holding tank utilized by the 60K RO system. This feedwater is then transferred by a centrifugal pump to the 4K RO unit. Sulfuric acid is added to adjust the feed pH to 2.9 in order to maintain iron constitutents in solution and control iron fouling of the membranes. If a precipitation inhibitor is to be used, it is also added at this point. The feed is then filtered in the 10-micron cartridge filters to remove any suspended solids.

The feed pressure to the unit is controlled by passing a portion of the feed through a valved bypass line. The overall unit recovery is adjusted by altering the amount of the brine to be recycled with the fresh feed to the unit, where increasing the brine recycle also increases the unit recovery of product water. The resulting product water is pH adjusted to 6.5 before it is discharged to the drain. The waste brine is lime neutralized, or it may be used as feed to another process.

The 4K RO unit operations are discussed in further detail in Sections 6, 7, and 8 which document studies performed to evaluate precipitate inhibitors, neutrolosis processes, and the coupled IX/RO treatment system.

TWIN-BED ION EXCHANGE SYSTEM

Equipment

The heart of this system is a twin-bed sodium-form IX unit manufactured by Culligan International Company. It consists of two pressure tanks, 0.61 m (24 inch) in diameter and 2.43 m (8 ft) high, each containing 0.41 m^3 (14.5 ft^3) of resin. The tanks are hot rolled steel rated at 690 kN/m^2 (100 psi) with a 0.1-mm vinyl-ester lining for corrosion resistance. This unit is shown in Figure 12.

To maintain continuous operation, an automatic hardness sensing device of the chemical titration type is used to monitor the leakage in the effluent. This hardness monitor senses a pre-set level of leakage and provides a signal to switch from one bed to the other when the breakthrough point is reached. Regeneration of the exhausted bed can be initiated automatically, either by the monitor or manually. In addition, the duplex IX system, when operating in the coupled IX/RO mode, can utilize both Na_2SO_4 loaded waste

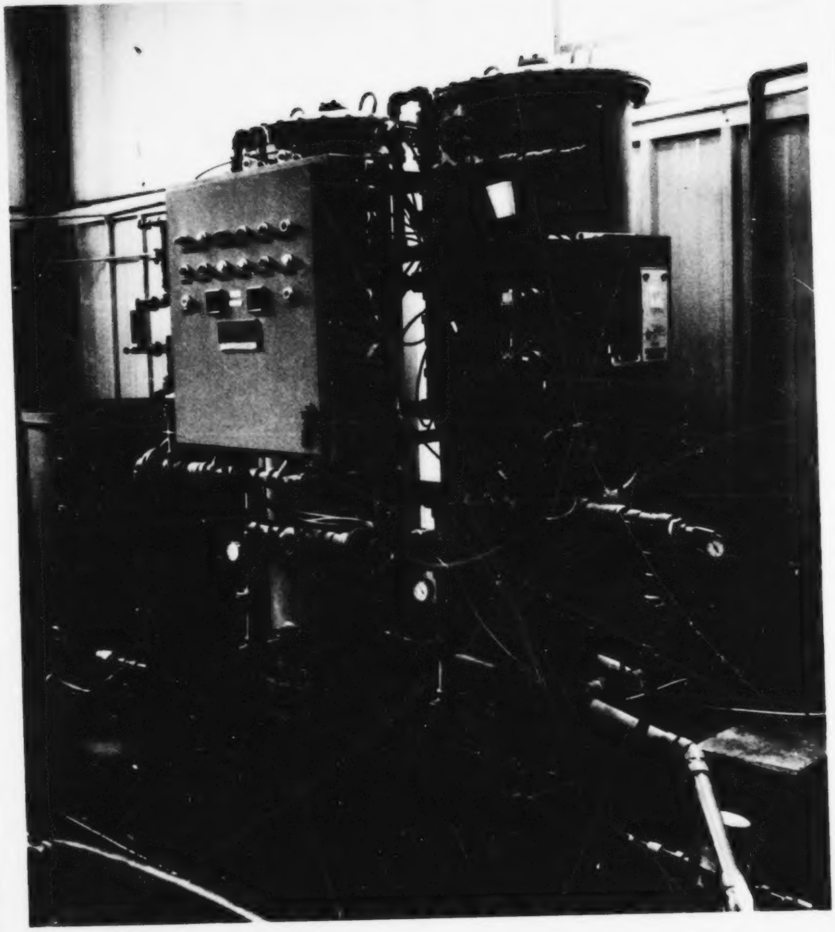

Figure 12. Twin-bed CIX system.

brine from the 4K RO unit and pure NaCl solution as a regenerant. An appropriate valve system provides the capability to transfer regenerant to the resin beds from either an 1893-l (500-gal) RO brine holding tank or a 757-l (200-gal) sodium chloride solution storage vessel.

Process Description

AMD feed is transferred to the IX unit from the indoor holding tank by means of a centrifugal pump. Before the AMD is fed to the IX column in service, its pH is adjusted to 2.8 by addition of sulfuric acid in order to prevent iron precipitation in the resin bed. The AMD passes through the servicing exchanger at a flow rate of 0.22 to 0.25 lps (3.5 to 3.9 gpm).

During the downflow exhaustion process, samples of softened water from the ion exchanger are taken at intervals to obtain leakage and free mineral acidity (FMA) data. In addition, a representative sample (AMD composite) of the average influent water to the resin is continually collected at hourly intervals throughout the entire exhaustion run. This composite sample is used to calculate the average cationic loading to the CIX, and with the total service time, is used to compute the IX capacity.

After the exhaustion process of the in-service IX column is completed, the alternate tank on standby simultaneously goes into service, thus maintaining a continuous AMD treatment process. The exhausted ion exchanger is then backwashed by sending a strong flow of AMD upward at the rate of 1.0 - 1.1 lps (16-18 gpm). It is subsequently regenerated by a specified amount of sodium chloride solution and/or Na_2SO_4 brine at a flow rate of 0.27 lps (4.3 gpm) in the downflow direction. After the regenerant has passed through the resin, a slow rinse, followed by a fast rinse, is applied to complete the regeneration cycle and return the exchange resin bed to a standby service mode. The operation is classified as co-current, since it utilizes both regeneration and exhaustion in a downflow mode.

Further details of these procedures are presented in Section 8.

NEUTRALIZATION SYSTEMS

In certain RO and neutrolosis studies, it was necessary to have outdoor aeration and clarification capability in addition to RO, neutralization, aeration, and clarifier equipment inside the pilot plant facilities building.

The aerator outside the building is a surface aerator with a holding basin made of concrete. The basin has a capacity of approximately 7600 l (2000 gal), and depending upon the brine flowrate, it may provide a residence time of two to ten hours. Figure 13 is a photograph of this aerator.

The clarifier is a steel tank of 37,900-l (10,000-gal) nominal capacity. It is constructed above ground, near the aerator, and provides a residence time of ten to fifty hours, again depending upon the brine flow rate. Figure 14 shows the clarifier beyond the surface aerator.

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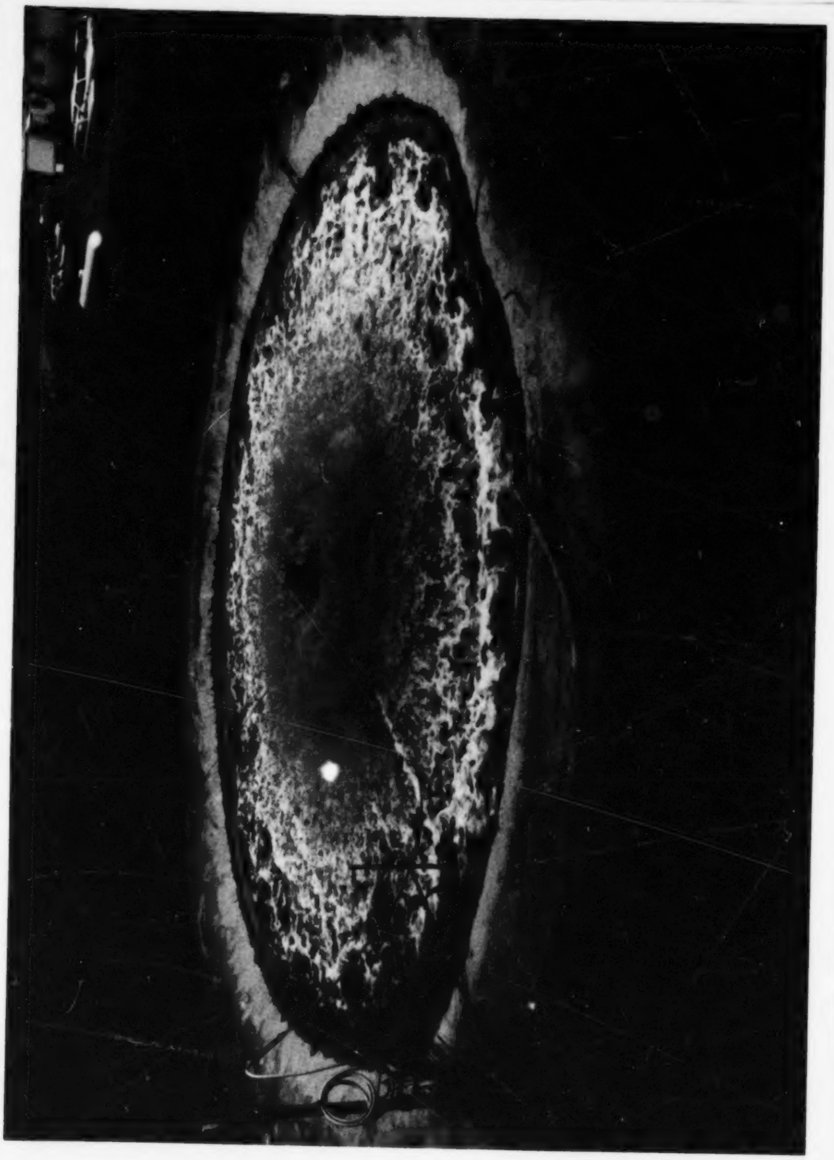

Figure 13. Outdoor 7600-liter (2000-gallon) surface aeration system.

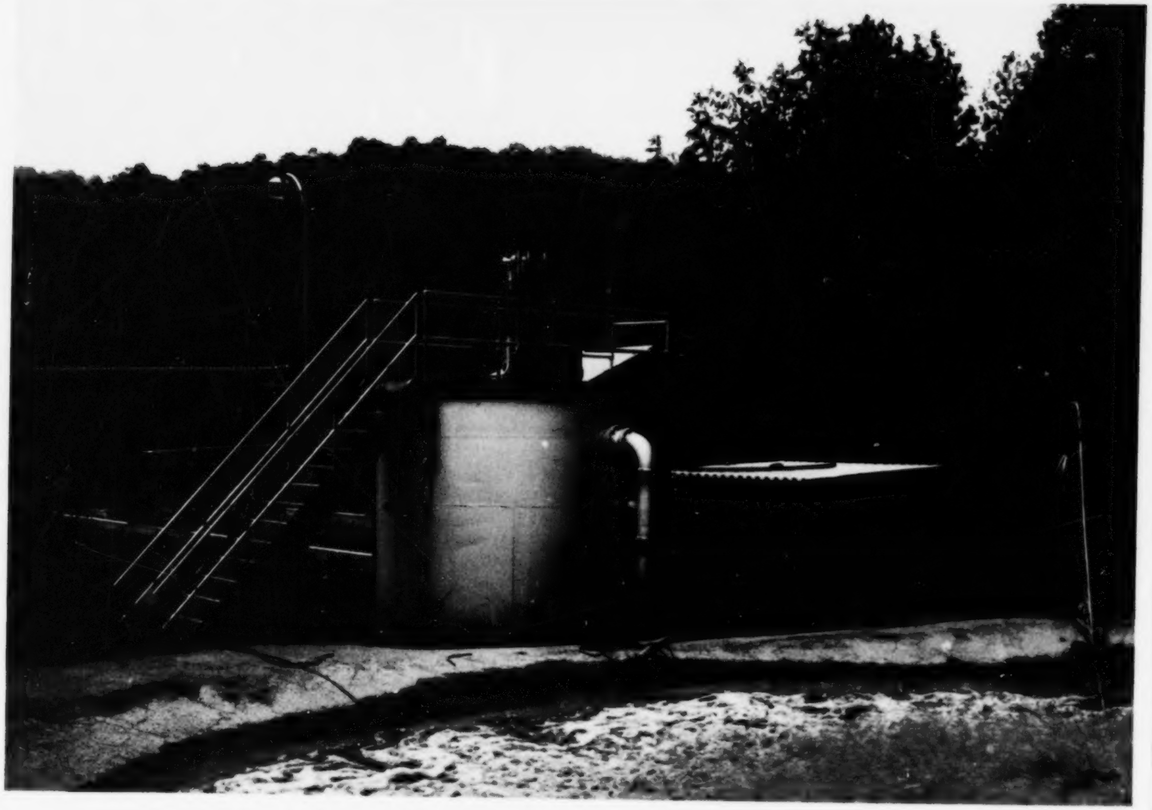

Figure 14. Outdoor 37,900-liter (10,000-gallon) clarifier.

SECTION 6

REVERSE OSMOSIS SYSTEMS OPERATIONS

One major aspect of the work conducted at the Crown Mine Drainage Control Field Site was the examination of RO pilot plant performance under a variety of AMD feed conditions. Studies focused on the production of high quality permeate from Crown AMD using the 60K RO unit at 50-to 90-percent recovery levels, the investigation of chemical pretreatment of AMD to alleviate or retard precipitate fouling of RO membranes, and the documentation of operation and maintenance problems (including repair efforts) created by long-term, sustained usage of RO equipment in the field. Prior to discussing experimental procedures and results, a short overview of RO process principles relevant to studies conducted at Crown is presented.

PRINCIPLES OF REVERSE OSMOSIS

RO is a process that utilizes a semi-permeable membrane through which almost pure water (permeate) is transported from a concentrated solution (brine) to a dilute solution by applying a pressure which is greater than the natural osmotic pressure. Since the membrane essentially rejects (is impermeable to) the dissolved ions, they are retained in the concentrated brine solution. In this manner a feed such as AMD can be demineralized to produce a quantity of permeate separated from a volume of concentrate that contains almost all of the pollutants originally present. The water flow rate (flux) through the membrane is proportional to the difference between the net applied pressure and the natural osmotic pressure of the concentrate, while salt transport across the membrane surface depends primarily on the salt concentration gradient which is relatively independent of the pressure. These relationships can be expressed as

$$Q_1 = A_1 (\Delta P - \Delta \pi) \tag{1}$$

$$Q_1 = A_2 (C_b - C_p), \tag{2}$$

where $Q_1 \equiv$ permeate flux, liter/m^2-day (g/cm^2-sec)

$Q_2 \equiv$ salt flux, kg/m^2-day (g/cm^2-sec)

$A_1 \equiv$ water permeability constant (membrane), liter/m^2-day-kN/m^2 (g/cm^2-sec-atm)

$A_2 \equiv$ salt permeability constant (membrane), m/day (cm/sec)

ΔP ≡ net applied pressure*, kN/m^2 (atm)

$\Delta \pi$ ≡ osmotic pressure difference, kN/m^2 (atm)

C_b ≡ salt concentration in concentrate, kg/m^3 (g/cm^3)

C_p ≡ salt concentration in permeate, kg/m^3 (g/cm^3).

Equation (1) appears to indicate that permeate flux through the membrane is increased as the applied pressure is increased. However, a counter-effect occurs, i.e. as the salt concentration of the brine is increased, with increasing permeate flow, the osmotic pressure is raised, and this in turn tends to reduce permeate flux. Thus, it is the magnitude of $\Delta P - \Delta \pi$ which ultimately governs permeate flow rates.

The membrane is truly the key component of an RO system. Many variables can affect membrane performance, and therefore RO performance.

Water Recovery

As noted above, when a feed water under applied pressure continuously moves through an RO unit, water is transported through the membrane. This results in an increase in the salt concentration of the water not passing through the membrane. The percentage of the feedwater collected as a permeate is defined as the recovery (γ).

It is found that the product water quality is degraded with increasing water recovery due to the increasing difference between C_1 and C_2 across the membrane [Equation (2)]. Therefore, the maximum water recovery obtainable may be limited by the product quality desired. For an RO system, the final brine concentration (C_b) is approximately related to the final feed concentration (C_f) by

$$(C_b/C_f)_{final} = \frac{1}{1 - \gamma}, \qquad (3)$$

where γ is the decimal equivalent of the recovery.

It can be seen, for example, that at 90-percent permeate recovery, the brine concentration is ten times that of the original feed. Thus, attempts to attain high product recoveries can cause problems with respect to product quality deterioration, elevated osmotic pressure, thus necessitating ever-increasing feed pressures to maintain a constant product flow rate.

Brine Flow Rate

When water is transported across the membrane in an RO process, almost all of the pollutant salts are left on the brine side of the membrane, and a boundary layer with high salt concentrations is formed at the membrane surface. The ratio of the salt concentration at the membrane surface to that in the bulk concentrate stream is defined as the concentration polarization ratio. This concentration polarization phenomena acts to exacerbate the effects of a high solute concentration in the brine channel, namely, higher salt leakage and possible membrane fouling.

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*The net applied pressure is the difference between the pressure applied to concentrate side of the membrane and that pressure existing on the permeate side of the membrane.

The severity of concentration polarization effects can be minimized by increasing the flow rate of concentrate in the membrane-module brine channel. However, because high brine flows tend to erode the membrane and shorten its useful life, membrane manufacturers generally recommend a flow rate range which reflects a balance between reduced concentration polarization and shortened membrane life. The proper brine flow rate can be maintained by a tapered vessel array, as in the 60K and 4K RO units, and by recycling brine (if necessary) in low product output RO units having only a few pressure vessels. The recycle of brine raises the average solute concentration in the unit, which in turn can adversely affect the RO system performance as mentioned previously.

Feed pH

Over a long period of time, cellulose acetate membranes are hydrolyzed by the water which comes in contact with them. It has been found that pH has a profound impact on the rate at which the hydrolysis occurs and that the hydrolysis rate is minimized at a pH of 5.0 to 5.5 (20).

In the case of AMD treatment, it has been common practice in previous RO operations to acidify the feed to pH 2.8 in order to prevent the precipitation of ferric iron in the RO unit. This necessitates a trade-off of membrane life against the prevention of performance deterioration due to membrane fouling.

Feed Temperature

Feed temperature is also an important parameter in determining the permeate flow and the membrane hydrolysis rate. Data presented by Gulf General Atomics, Inc. (20) indicated that the permeate flux increases with temperature, and that the flux is altered by five percent of the flux at 25° C for each $\Delta T = 2°$ C change in the temperature. In practice, the feed temperature should be maintained below 30° C in order to obtain reasonable membrane life. In some cases it might be necessary to provide feed cooling capability to maintain the feed temperature at acceptable levels.

Precipitate Fouling of Membranes

It was previously noted that pH control is necessary in RO treatment of AMD to prevent precipitation of ferric iron on the membranes. However, there is also a problem with moderately soluble salts, principally calcium sulfate in AMD, which cannot be controlled as easily. Generally, the maximum permeate recovery is limited by the solubility of such salts. For example, if a solute is present in the feed at fifty percent of its saturation concentration, only fifty percent of the feed can be recovered as permeate before the concentrate is saturated with the salt. Further concentration would result in solute precipitation. Since concentration polarization causes the highest concentration to appear at the membrane surface, and because the membrane also acts to promote precipitation, moderately soluble salt precipitates tend to form a deposit on the membrane. This deposited layer, which is rather impermeable to water flow, reduces the membrane and RO system performance. Thus, it is desirable to have methods to predict the maximum system recovery based on the behavior of moderately soluble salts present in the feed, or to develop techniques to inhibit the formation of precipitate. Predictive methods of solubility are discussed in Appendix B in conjunction with the neutrolosis models, whereas precipitation inhibitor studies are presented later in Section 6.

RESULTS OF EXPERIMENTAL STUDIES

60K RO System Performance-Initial 10-Day 50-Percent Recovery Shakedown Study

A 10-day shakedown test and initial evaluation of 60K RO system performance at nominal 50-percent recovery began on May 1, 1973 and was terminated on May 11, 1973. The operation of the unit was carefully monitored on a round-the-clock basis to permit close evaluation of performance data and operational problems. What follows illustrates the methods of data acquisition and analysis used throughout the course of RO systems investigations.

Although it was intended that the unit be operated for 10 continuous days without shutdown, two shutdown periods were experienced. The first lasted 3¼ hours on May 5, and was due to a power outage at the AMD bore hole pump. The second, which occurred on May 10, was of 12 minutes duration, and was caused by a low pressure shut-off during a cartridge filter replacement. In both instances unit restart-up was accomplished without difficulty, with a rapid attainment of the operating parameters that existed just prior to the shutdown.

It was believed that brine conductivity could be maintained at 6000 µmhos/cm without causing an onset of calcium sulfate fouling in the second pressure vessel bank of the 8-6 tube bank arrangement. This proved to be true; but in order to operate at this brine conductivity level, it was necessary to incorporate product recycle to generate a blended feed having conductivity the order of 3,300 µmhos/cm. This additionally provided the opportunity to check out the operational characteristics of the product recycle system. During the course of the shakedown test, it was necessary to adjust the product recycle flow rate between 0.76 and 1.13 lps (12 and 18 gpm) in order to compensate for varying qualities in the acid mine feedwater, which tended to cause corresponding deviations in brine conductivity from 6,000 µmhos/cm.

It was noted that the 60K RO system was capable of maintaining the following operational parameters at almost constant levels throughout the course of the 10-day run:

Pump discharge pressure: 4,690 kN/m^2 (680 psi)
Blended feed pH: 2.9
Acidified product water pH: 2.9
Total feed flow rate: 5.23 to 5.30 lps (83.0-84.1 gpm)
Brine flow rate: 2.63 lps (41.7 gpm)
Total product flow rate: 2.52 to 2.60 lps (40.0-41.3 gpm).

There is a slight discrepancy in the flow rate data cited above, namely that the sum of the brine flow and total product flow is in the order of 0.07 to 0.08 lps (1.1-1.3 gpm) less than the total feed flow. This is because the brine flow and total feed flow rates had to be estimated from the flow controller indicators, whereas the total product flow rate could be rather accurately determined by measured volume flow rates from individual pressure vessels.

During the 10-day test period average product flow rates from the eight Bank No. 1 tubes were 0.19 lps (3.03 gpm) per module, and from the six Bank No. 2 tubes 0.17 lps (2.74 gpm). This yielded a 10-day average product flow of 2.56 lps (40.68 gpm), which is approximately 220,000 lpd (58,000 gpd) and close to the rated output of the unit. TABLE 3 presents a typical set of flow, pressure, and recovery data taken after 184 hours of RO unit operation. Note that the lower average flow rate from Bank No. 2 tubes is as expected since they "see" a lower average feed pressure and experience a higher osmotic pressure than Bank No. 1 spiral-wound membranes.

Feed inlet pressures ranged from 3,410-3,490 kN/m^2 (495-500 psi) at the beginning of the run to 3,480-3,510 kN/m^2 (505-510 psi) at the conclusion of the test. Since the unit is designed to provide a constant product output, this increase in pressure was attributed primarily to membrane compaction. During the period May 3 - May 11, data was collected and computations made (including osmotic pressure corrections) to determine changes in the water permeability coefficients for both tube banks. The results of these calculations are shown in TABLE 4. Standard analysis of the log-log plot of water permeability coefficients versus time indicated a slope of -0.03 during the eight-day period, a quite tolerable value (20).

The product water conductivity varied from 50 μmhos/cm to 80 μmhos/cm throughout the 10-day shakedown run. Chemical analyses of blended feeds and product water showed that the rejection capabilities of the membranes exceeded those of the design specifications. A representative set of water quality data taken 184 hours after unit start-up is shown in TABLE 5.

After 243.5 hours of operation, the system was manually shut down and backflushed with a pH 2.5 phosphoric acid solution.

The overall performance of the 60K RO unit operating at a nominal 50 percent unit recovery was in accordance with design specifications, with regard to both a constant rated product water output of 227,000 lpd (60,000 gpd) and product water quality, as evidenced by measured percent

TABLE 3. OPERATIONS SUMMARY FOR 60K RO UNIT SHAKEDOWN RUN @ 184 HOURS (49.0 PERCENT UNIT RECOVERY)

Pressure and Flow	Individual Tube Product Flow, lps (gpm)
Pump Discharge Pressure	Tube No. 1 - 0.195 (3.09)
4,680 kN/m^2 (680 psi)	Tube No. 2 - 0.196 (3.11)
Feed Inlet Pressure	Tube No. 3 - 0.191 (3.03)
3,510 kN/m^2 (510 psi)	Tube No. 4 - 0.199 (3.16)
ΔP Across 8 - 6 Array	Tube No. 5 - 0.189 (3.01)
267 kN/m^2 (38.8 psi)[a]	Tube No. 6 - 0.203 (3.23)
ΔP Across Bank #1	Tube No. 7 - 0.182 (2.89)
138 kN/m^2 (20.0 psi)[a]	Tube No. 8 - 0.186 (2.96)
ΔP Across Bank #2	Tube No. 9 - 0.170 (2.70)
137 kN/m^2 (19.9 psi)[a]	Tube No.10 - 0.180 (2.86)
Blended Feed Flow	Tube No.11 - 0.170 (2.70)
5.30 lps (84.1 gpm)	Tube No.12 - 0.177 (2.82)
Raw AMD Feed Flow	Tube No.13 - 0.170 (2.70)
4.23 lps (67.1 gpm)[b]	Tube No.14 - 0.185 (2.94)
Product Recycle Feed Flow	
1.07 lps (17.0 gpm)	Recovery:
Brine Flow	Reverse Osmosis Unit - 49.0%[d]
2.70 lps (42.9 gpm)	Total Process - 36.1%[e]
Total Product Flow	
2.60 lps (41.2 gpm)[c]	

[a] The ΔP quantities are the results of three separate measurements, which explains the slight difference between the sum of the individual Bank #1 and Bank #2 readings and the ΔP measurement across the entire 8-6 array (Banks #1 and #2).

[b] There is no direct measurement of Raw AMD Feed Flow. It is taken to be the difference between Blended Feed Flow and the Product Recycle Feed Flow.

[c] The Total Product Flow is the sum of the individual Tube Product Flow measurements (Note that 41.2 gpm = 59,300 gpd)

[d] Recovery for the Reverse Osmosis Unit is defined as:

$$\frac{\text{Total Product Flow}}{\text{Blended Feed Flow}} \times 100\%$$

[e] Recovery for the Total Process is defined as:

$$\frac{(\text{Total Product Flow} - \text{Product Recycle Feed Flow})}{\text{Raw AMD Feed Flow}} \times 100\%$$

TABLE 4. WATER PERMEABILITY COEFFICIENTS (A_1) FOR BANKS #1 AND #2, 60K RO UNIT SHAKEDOWN RUN @ 184 HOURS

Hours of Unit Operation	A_1 - Bank #1 liter/m^2-day-kN/m^2 (10^{-5} gm/cm^2-sec-atm)	A_1 - Bank #2 liter/m^2-day-kN/m^2 (10^{-5} gm/cm^2-sec-atm)
46.4	0.1224 (1.436)	0.1232 (1.445)
70.4	0.1192 (1.398)	0.1175 (1.378)
94.4	0.1203 (1.411)	0.1199 (1.406)
118.4	0.1181 (1.385)	0.1186 (1.391)
142.4	0.1194 (1.401)	0.1175 (1.378)
166.4	0.1162 (1.363	0.1160 (1.361)
190.4	0.1172 (1.375)	0.1182 (1.386)
214.4	0.1151 (1.350)	0.1139 (1.336)
238.4	0.1159 (1.360)	0.1172 (1.375)

[*] To convert from liter/m^2-day-kN/m^2 to gm/cm^2-sec-atm multiply by 1.17358×10^{-4}

TABLE 5. CHEMISTRY ANALYSIS FOR 60K RO UNIT SHAKEDOWN RUN @ 184 HOURS

	Raw Feed	Blended Feed	Brine	Product	Percent Rejection[a]
Conductivity, μmhos/cm	3800	3600	6300	48	98.7
pH	4.7	3.1	2.9	3.8[b]	-
Acidity (as $CaCO_3$ to end point pH 7.3) mg/l	930	870	1520	132	84.8
Ca, mg/l	430	310	660	1.5	99.5
Mg, mg/l	140	100	200	0.5	99.5
Total Fe, mg/l	390	290	570	1.5	99.5
Fe^{2+}, mg/l	390	290	560	1.2	99.6
Na, mg/l	460	380	740	3.2	99.2
Al, mg/l	29	22	44	0.02	99.9
Mn, mg/l	6.8	5.3	9.5	0.02	99.6
SO_4, mg/l	3400	2700	5100	16	99.4
TDS, mg/l	4850	3800	7300	23	99.4

[a] $$\text{Percent Rejection} = \frac{\text{Blended Feed Conc. (mg/l)} - \text{Product Conc. (mg/l)}}{\text{Blended Feed Conc. (mg/l)}} \times 100\%$$

[b] Product pH exiting RO unit prior to recycle and acidification

ion rejections at membrane surfaces.* All pumps, control systems, and flow and water quality instrumentation appear to have functioned properly. Also, product water recycle and automatic backflushing systems operated effectively.

60K RO System Performance - 50 to 90 Percent Unit Recovery Operations

During the period May 1973 to October 1973, the 60K RO unit was operated for a total of 1,150 hours, primarily to check out system performance at pressure vessel arrays and nominal recoveries of 50, 60, 70, 75, 80, 85 and 90 percent. Information concerning the treatment plant and operational procedures associated with the RO unit are given in Section 5.

To avoid the possibility of $CaSO_4$ fouling of RO membranes at once-through (no product recycle) recoveries greater than 45 percent, it was deemed necessary to recycle portions of the RO product output to the raw AMD feed stream to generate a blended feed having sufficiently low concentrations of calcium and sulfate to permit high recovery operations. In order to minimize the chances of fouling the RO unit during the various recovery check-outs of the system, efforts were made to adjust flow rates to maintain the waste brine conductivity below a newly set limit of 8,000 μmhos/cm; however, this limit was exceeded when operating at 90 percent recovery (with no apparent ill effects). Representative flow rates for raw feed, blended feed, brine, overall product output, and product recycle are given in TABLE 6, and chemistry analyses for 60-through 90-percent recovery operations are given in TABLES A-1 through A-7 in Appendix A. Information showing product flux variations for individual tube banks during the 1,150-hour check-out period is shown in Figures 15 and 16. During all runs, the blended feed pH was kept between 2.5 and 3.1 to minimize iron fouling, with the optimum range being pH 2.8-3.0 both to ensure no iron precipitation and lessen sulfuric acid consumption, recognizing this might have a deleterious effect on membrane lifetime.

There were no significant declines in tube product flux throughout the 1,150-hour set of runs--with the exception of Tube 6 at greater than 75-percent unit recovery. At the 85-percent recovery point the modules in Tube 6 were replaced, since this vessel is the last one in the 5-4-2-2-1 array, and must process a feed stream containing the highest concentration of dissolved solids. Examination of the original Tube 6 modules showed no evidence of $CaSO_4$ fouling, and flux decline was attributed to the increased osmotic pressures which exist in the last bank at the highest recoveries. It should be noted that with the 60K RO unit designed to operate at a preset product output, feed pressures are automatically adjusted to drive more water through the early banks as compensation for reduced output of the latter banks.

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*To minimize the possibility of calcium sulfate precipitation on the membrane surface, raw AMD was blended with RO product water to reduce the calcium concentration in the blended feed to approximately 300 mg/l. This resulted in an average overall process recovery of 36 percent (See TABLE 3).

TABLE 6. FLOW RATES FOR 60K RO UNIT OPERATIONS (60 - 90 PERCENT RECOVERY)

Item	Result							
Nominal Unit Recovery (%)	50	60	70	75	75	80	85	90
Actual Unit Recovery (%)	49.0	59.7	69.6	73.6	73.6	80.0	85.4	90.3
Flow Rates, lps (gpm)								
Raw Feed	4.23 (67.1)	2.80 (44.4)	2.08 (32.9)	1.67 (26.5)	26.5 (19.2)	19.2 (13.1)	0.83 (13.1)	0.58 (9.2)
Blended Feed	5.30 (84.1)	4.44 (70.4)	3.82 (60.5)	3.53 (56.0)	3.53 (56.0)	3.15 (49.9)	3.03 (48.1)	2.91 (46.2)
Brine	2.70 (42.9)	1.79 (28.4)	1.16 (18.4)	0.93 (14.8)	0.93 (14.8)	0.63 (10.0)	0.44 (7.0)	0.28 (4.5)
Product	2.60 (41.2)	2.65 (42.0)	2.66 (42.1)	2.60 (41.2)	2.60 (41.2)	2.52 (39.9)	2.59 (41.1)	2.63 (41.7)
Product Recycle	1.07 (17.0)	1.64 (26.0)	1.74 (27.6)	1.86 (29.5)	1.86 (29.5)	1.94 (30.7)	2.20 (35.0)	2.33 (37.0)
Pressure Vessel Array	8-6	7-4-3	7-4-3	7-4-3	5-4-3-2	5-4-3-2	5-4-2-2-1	5-4-2-2-1

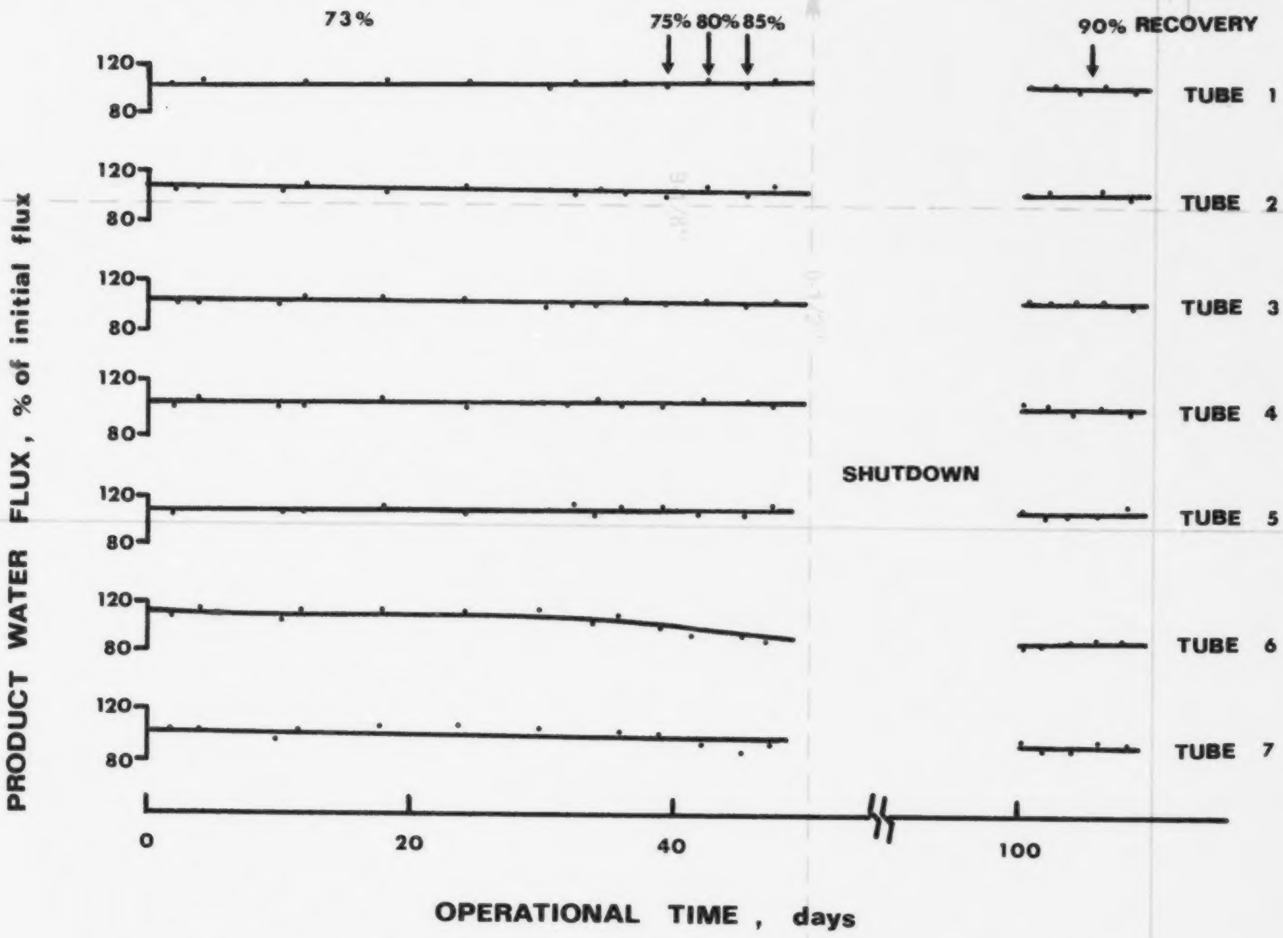

Figure 15. Flux behavior of 60K RO unit at various recovery levels (tubes 1-7).

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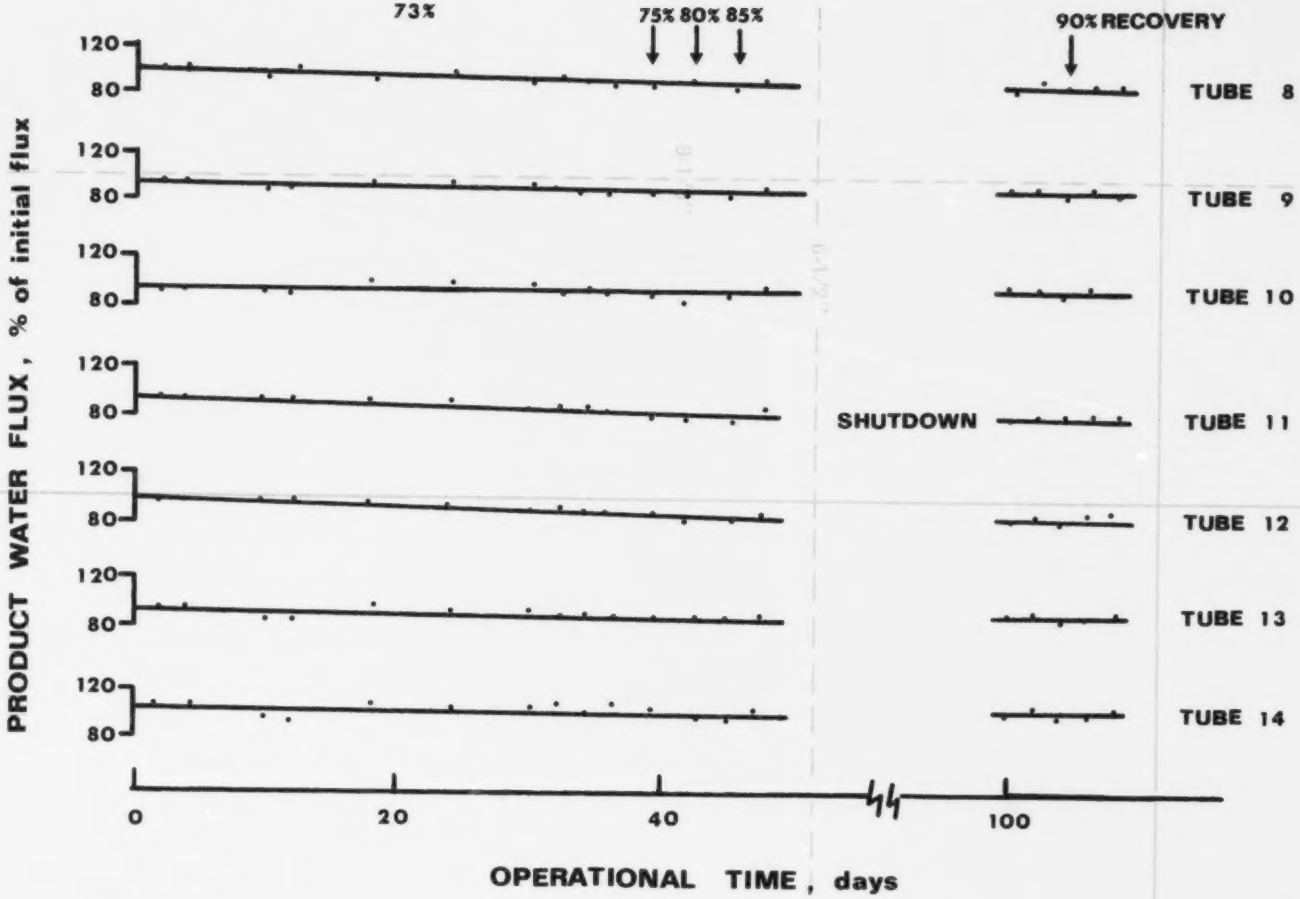

Figure 16. Flux behavior of 60K RO unit at various recovery levels (tubes 8-14).

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TABLES A-1 through A-7 showed that membrane rejection levels based on blended feed composition were generally greater than 98 percent for ions at all recoveries, other than aluminum and sodium which tend to experience slightly lower rejections by the RO membrane. This was in agreement with observations noted by other investigators working with cellulose acetate RO membrane systems for AMD treatment. The product water was of nearly potable quality except for low pH, and perhaps a bit too much iron, which could be "tasted" at levels greater than 1 mg/l. Polishing the product water with lime or caustic soda could correct both the pH and iron taste problems.

Brine Conductivity Fouling Studies

In order to deduce the maximum permissible brine conductivity of Crown AMD before the onset of membrane fouling in RO treatment processes, a 300-hour operation was conducted with the 4K spiral wound RO unit, which had been utilized by EPA for research studies at Norton, West Virginia. The results of this study are shown in Figure 17. The flux declines at 15-percent recovery during the first 180 hours of operation were due to membrane compaction. However, an uninterrupted transition to 36-percent recovery showed a rather steady flux decline at a brine conductivity of 7,500-8,000 μmhos/cm, which appeared to represent an upper limit for RO treatment of Crown AMD if serious membrane fouling by $CaSO_4$ precipitation was to be prevented.

It should be noted that Figure 17 is plotted on a linear scale instead of the commonly used log-log plot. During the course of many experimental runs at Crown, it was found that while log-log plots are satisfactory for following the progress of normal membrane performance loss over long time periods, such plots did not seem optimal for depicting severe membrane fouling situations. In such cases the flux-time curve does not appear to be a straight line on either a linear or a log-log plot, but the linear graph generally provides a reasonable (and sometimes dramatic) format for data presentation. For this reason, linear plots are used throughout this report for the graphing of data obtained from membrane fouling studies.

$CaSO_4$ Precipitate Inhibitor Studies

The potential for increasing RO systems recoveries by using chelate agents to act as $CaSO_4$ precipitate inhibitors was investigated using the 4K RO unit. Three such agents were tested: CL-14 and CL-50 furnished by Calgon Corporation, and L-39 supplied by Dowell, Inc. In all test runs the procedure was as follows:

1. Operate the RO unit for several days at low recovery to compact membranes in order to be able to differentiate flux decline due to membrane compaction from flux decline resulting from actual $CaSO_4$ membrane fouling.

2. Operate the RO unit using Crown AMD without additivies at recoveries in the range 50-75 percent which are known to create $CaSO_4$ fouling situations, and observe the flux decline in the

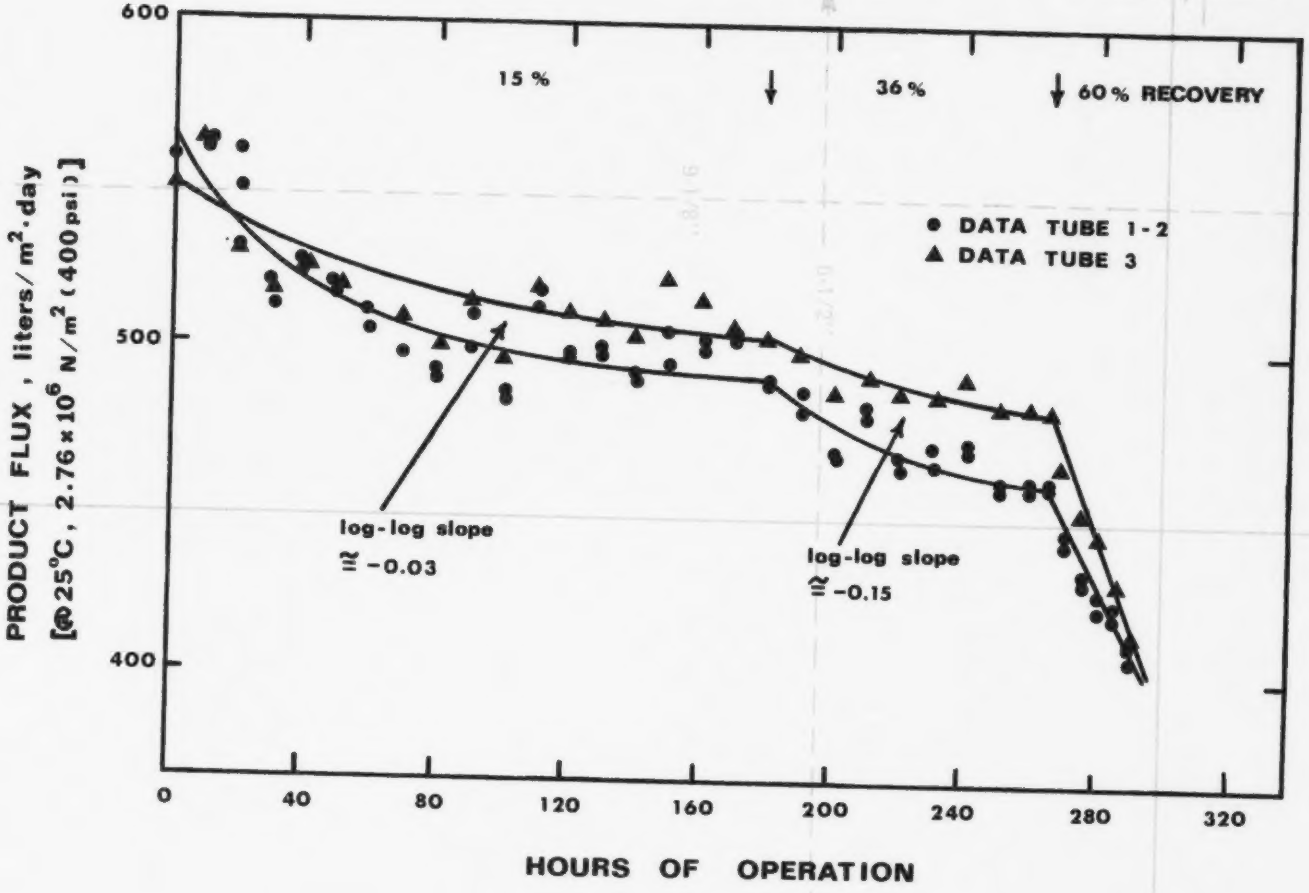

Figure 17. Brine conductivity fouling studies - 4K RO unit.

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last bank (Tube 3) over a period of several hours.

3. Flush the RO unit with pH 2.5 phosphoric or citric acid solution, and backflush with water for several hours to clean the membranes.

4. Repeat Step 1.

5. Repeat Step 3. with the addition of precipitate inhibitors under the same conditions as the run without additives.

6. Repeat Step 3.

Studies were made using the following dose of precipitate inhibitors in the raw AMD feed:

CL-14 (50 mg/l)
CL-50 (100 mg/l)
L-39 (5 & 10 mg/l).

The results of the CL-14 tests are shown in Figure 18 and 19. The baseline and inhibitor trials were operated at a system recovery of 65 percent. It is seen that the inhibitor did not reduce the rate of flux decline. The CL-50 tests were run at an RO recovery level of 60 percent. The data presented in Figures 20 and 21 indicated that the RO unit performance with the inhibitor was much worse than that without the inhibitor. It is possible that the inhibitor was forming some type of complex that was depositing on the membrane. Figures 22 - 25 indicated that operation with the L-39 additive, at manufacturer recommended concentrations, was equally disappointing. In fact, at additions greater than 10 mg/l the additive actually caused clogging at the 10-micron cartridge filters used to pretreat the 4K RO feed.

It was generally concluded that precipitate inhibitors tested were of marginal value in preventing gypsum fouling to any significant extent. In terms of chemical costs and the operation of an automatically controlled additive injection system, they are probably not worthy of future consideration. There is reason to believe that many chemicals touted as $CaSO_4$ precipitate inhibitors or gypsum scale removal agents were not intended for use in an RO-AMD type operation, and in fact actually break down and become ineffective in the "under pH 3" environment of the RO system. However, because these are proprietary compounds, their exact chemical action and mechanisms for inhibiting the precipitation could not be determined.

Iron Fouling Studies

Three attempts were made to operate the 60K RO unit without acidification of the blended feed to pH 3.0 or lower. All proved unsuccessful, as fouling in the first bank caused the pressure drop across the bank to increase by 10 psi over a period of 20 hours. Normal ΔP (approximately 20 psi) was always restored across the first bank by phosphoric acid backflushing and product water rinsing procedures following completion of each test run.

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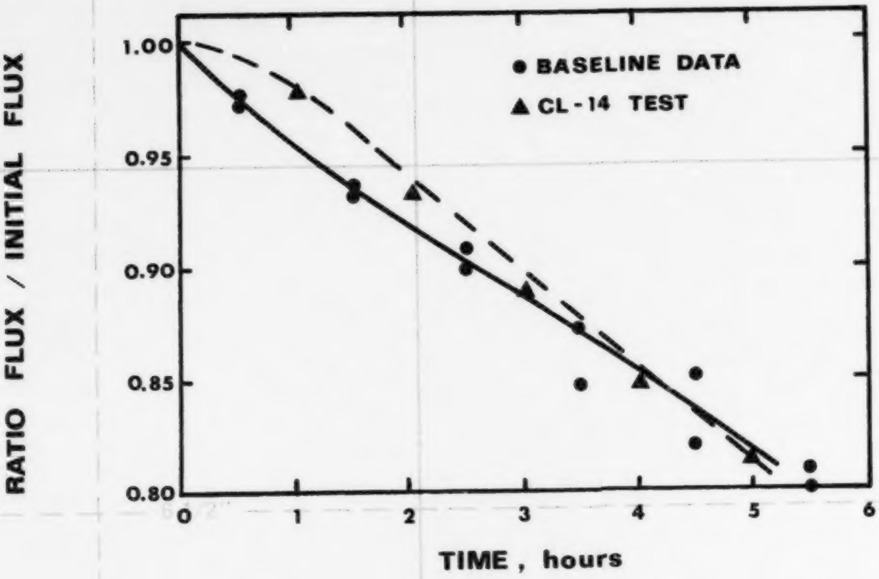

Figure 18. Flux comparison - tubes 1 and 2, CL-14 test.

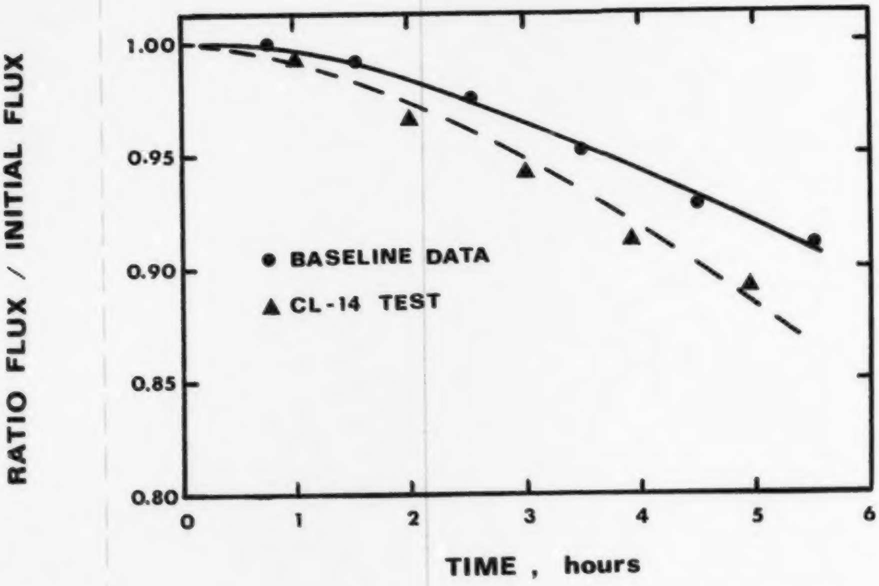

Figure 19. Flux comparison - tube 3, CL-14 test.

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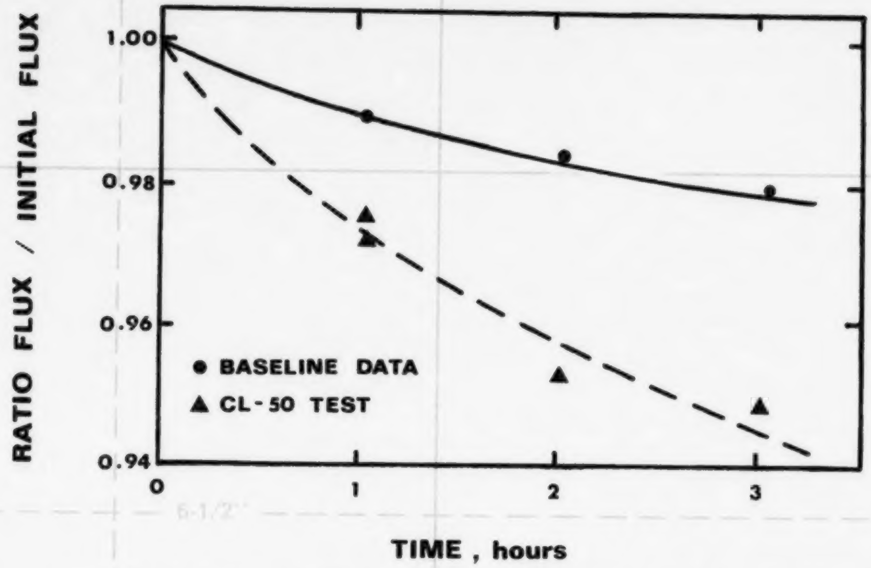

Figure 20. Flux comparison - tubes 1 and 2, CL-50 test.

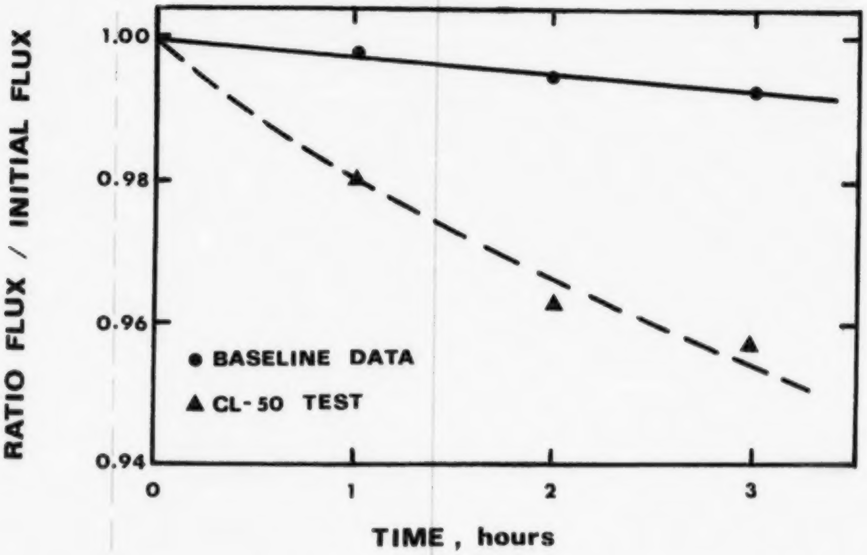

Figure 21. Flux comparison - tube 3, CL-50 test.

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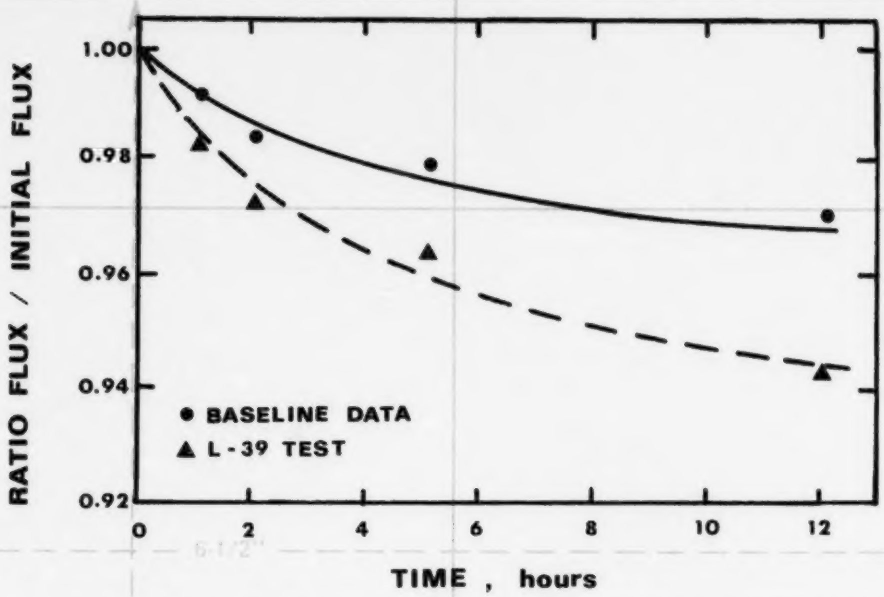

Figure 22. Flux comparison - tubes 1 and 2, L-39 test (5 mg/l).

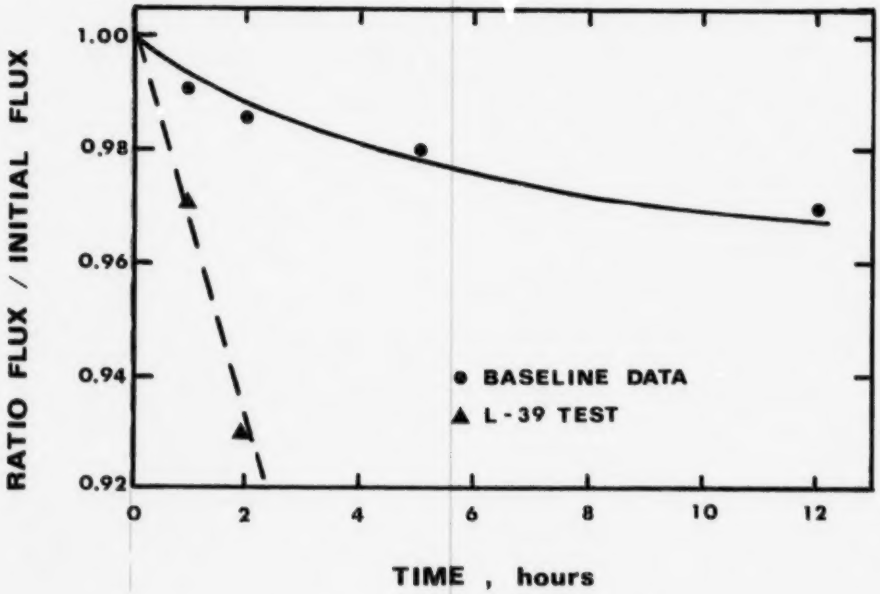

Figure 23. Flux comparison - tube 3, L-39 test (5 mg/l).

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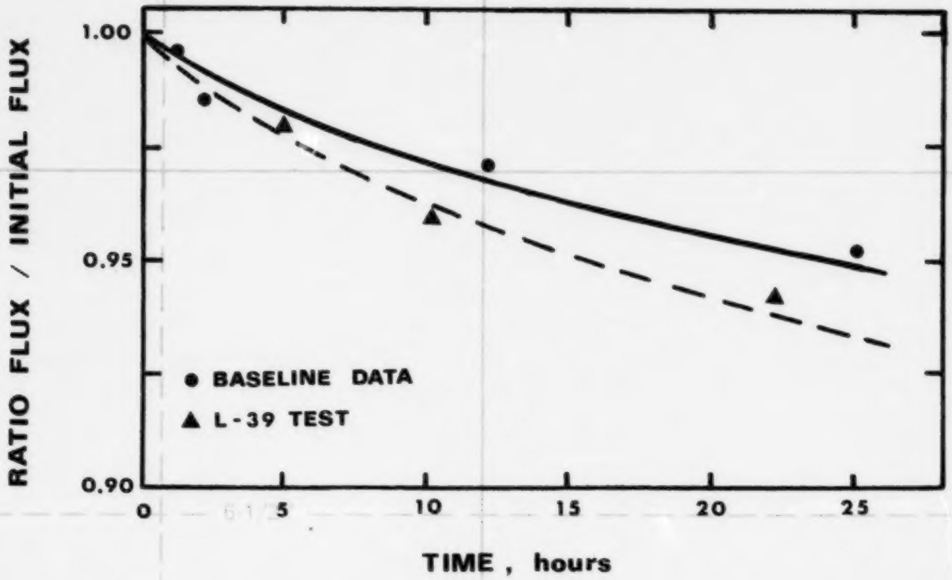

Figure 24. Flux comparison - tubes 1 and 2, L-39 test (10 mg/l).

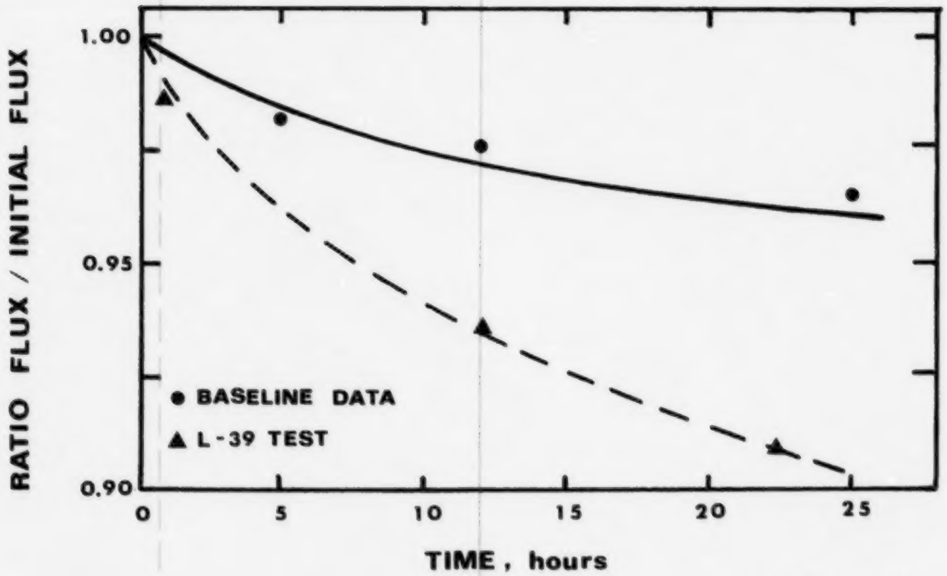

Figure 25. Flux comparison - tube 3, L-39 test (10 mg/l).

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Examination of sample modules from the first and second banks of the RO unit indicated that ferric iron had precipitated primarily on the first two or three modules in the first bank. There was little evidence of iron fouling elsewhere. The results of these tests merely verified the conclusions of previous investigators, namely that acidification of iron-laden AMD feed to an RO unit must be maintained at pH $\leq$ 3.0 to prevent ferric hydroxide precipitation within the system.

SUMMARY OF OPERATIONS AND MAINTENANCE EXPERIENCES - 60K RO UNIT

During the 1,150-hour 50-90 percent recovery checkout operation with the 60K RO unit, operational difficulties were minor in nature: a leak in the product water recycle pump, sticking of the brine flow controller, a malfunction of the product recycle rotameter, and several low suction pressure shutdowns due to loss of raw AMD feed at the bore hole. In all cases of automatic shutdown due to low (< 10 psig) feed pressure, the automated backflushing operations with pH 2.5-3.0 phosphoric acid solution functioned well, as evidenced by the return to pre-shutdown operating conditions (flow rates, system pressures, water quality) when the RO unit was restarted.

Throughout the two-year period of AMD treatment studies, one major problem developed; namely, the occurrence of corrosion defects in the stub tubes of the pressure vessels which forced numerous 60K RO system shutdowns due to pin-hole type leaks in the vessels. The feed-brine entry-exit ports on each pressure vessel are welded at right angles to the vessel itself. Although the pressure vessels and stubs are constructed of epoxy-coated carbon steel, it appeared that erosion of the epoxy coating occurred first in the stub tube. This was followed by metallic corrosion, which resulted in severe metal loss on the inner walls of the stub tube and small holes at the outer surface. As each erosion-corrosion problem appeared, the RO unit was shut down, and the defect corrected by spot-welding, surface grinding, and re-application of epoxy.

Repairs for the most part were satisfactory; however, the incidence of erosion-corrosion defects continued to accelerate during the course of the two-year investigations. The vendor has noted that another of its RO units, having identical pressure vessel design and being utilized in brackish water treatment, was experiencing erosion-corrosion problems similar to those at Crown. The vendor's recommendation was that newly designed fiberglas pressure vessels having end entry-exit feed-brine ports be installed to replace the current pressure vessel system.

Some brief comments should be made concerning the performance and durability of the spiral-wound cellulose acetate membrane-modules used in the 60K RO unit. During more than 4,500 hours of operation, the RO unit experienced only four module failures due to cracks in the module casing. No modules had to be replaced because of inherent loss of membrane rejection capability. There were occasions when modules were removed and dissected to examine iron or gypsum fouling patterns, and other times when the central axis product tubes were broken due to improper loading procedures. When one considers the types of investigations being conducted which often resulted in potential $CaSO_4$ fouling situations and deliberate iron fouling of the membranes, and the numerous deliberate and unintentional shutdown, membrane cleaning, and start-up operations--the track record of modular durability, performance, and lifetime must be rated as excellent.

SECTION 7

COUPLED REVERSE OSMOSIS/NEUTRALIZATION STUDIES

RO treatment of AMD often produces a considerable volume of concentrate which must undergo treatment and disposal processes, even though a significant amount of the feed may be recovered as a high quality permeate. In the majority of applications of AMD treatment by RO, the RO unit most likely would be utilized as an adjunct to neutralization processes to produce a given quantity of high quality water for a particular purpose. The concentrate in this case subsequently would be treated in the neutralization/clarifier train before discharge to surface waters. However, if it was desirable or necessary to alleviate concentrate disposal problems, a possible solution might be to recycle some portion of the neutralized brine to the RO unit for additional treatment. Ideally, such a coupled technique could yield a high permeate recovery of the raw AMD and a small amount of waste effluent. In some cases, the only waste might be a sludge which could be dried or disposed of in a landfill.

Previous work with RO/neutralization processes was conducted by the EPA staff at Norton, West Virginia (5, 6). The name 'neutrolosis' was applied to the coupled process in which the RO concentrate was lime neutralized and recycled to the RO unit. Although the Norton study showed an overall systems recovery of greater than 98 percent, it was not clearly determined how a long-term neutrolosis operation would function with respect to calcium sulfate fouling within the process loop, nor was the overall feasibility of operating in a neutrolosis mode explicitly evaluated.

A major purpose of this study was to carefully examine neutrolosis concepts. Three variations of the coupled RO/neutralization process were studied using lime, soda ash, and combined lime-soda ash as the respective neutralizing agents. These processes were evaluated from both theoretical considerations and on the basis of experimental results.

LIME NEUTROLOSIS

Basic Principles

In the neutrolosis process, concentrate from the RO unit is reacted with lime to raise the pH of the concentrate to a specified level. The reactor effluent is then aerated to oxidize the iron to facilitate its removal, and subsequently clarified to produce a sludge and a low turbidity supernatant. A large portion of the supernatant is blended with the raw AMD for further treatment in the RO unit, which results in much of the concentrate being continuously recycled in the coupled system (Figure 26). A considerable amount of reported research exists concerning the lime neutralization of AMD (21-24). The basis for lime neutralization as a water treatment process is that lime reacts with several metals to yield fairly insoluble hydroxides. The lime addition raises the pH so that the solubility equilibrium is shifted and the metals are precipitated from the water. The reactions which occur during lime neutralization are:

$$\text{A)}\quad MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH_2)\downarrow + CaSO_4 \quad (pH > 10.8),$$

$$\text{B)}\quad MnSO_4 + Ca(OH)_2 \rightarrow Mn(OH_2)\downarrow + CaSO_4 \quad (pH > 9.5),$$

$$\text{C)}\quad Al_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Al(OH)_3\downarrow + 3CaSO_4 \quad (pH\ 5.5 - 6.5),$$

$$\text{D)}\quad FeSO_4 + Ca(OH)_2 \rightarrow Fe(OH)_2\downarrow + CaSO_4 \quad (pH > 9.0),$$

and with adequate aeration

$$\text{E)}\quad 2Fe(OH)_2 + H_2O + \frac{1}{2}O_2 \rightarrow 2Fe(OH)_3\downarrow \quad (pH > 3.5).$$

At this stage several points should be noted. The first is that iron is the only metal that can be removed without greatly raising the pH of the stream to be treated. This has indeed been the case in practice, as illustrated by chemistry analyses presented in TABLE 7. In the AMD neutralization studies the iron removal was better than 99-percent complete, but the removal of the other metals was not significant unless a pH greater than 10.5 was maintained in the neutralization reactor. Raising the pH of the RO concentrate to this level presents difficulties with the process, such as the increased quantity of neutralizing agent required. Second, if the original dissolved solids in sulfate form are not removed from the system either in precipitate form in the sludge or in a concentrate "blowdown," several consequences occur. The solutes will build up in the recycle loop until their saturation concentration is reached. During this "build-up" stage high concentrations of certain of the solutes will result. This, in turn, will mean increased concentrations of these metals in the product water, and increased osmotic pressure in the concentrate, thus lowering the effective driving pressure for product water removal in the RO unit.

Finally, all of the neutralization reactions form calcium sulfate as one of the products. In order to remove most of the reactable components in AMD waters, it would be necessary to add a considerable amount of lime, thus greatly increasing the calcium sulfate loading. For example, in a typical sample of Crown water more than 1.55 kilograms of hydrated lime must be added to each thousand liters of RO concentrate neutralized. This is enough to gypsum-saturate the water by itself, but when added to the calcium sulfate already present, a supersaturated condition arises. Such a highly saturated concentrate stream poses the great problem with a lime neutrolosis type of operation; namely, scaling of the membranes with gypsum when the recycle stream is introduced to the RO unit.

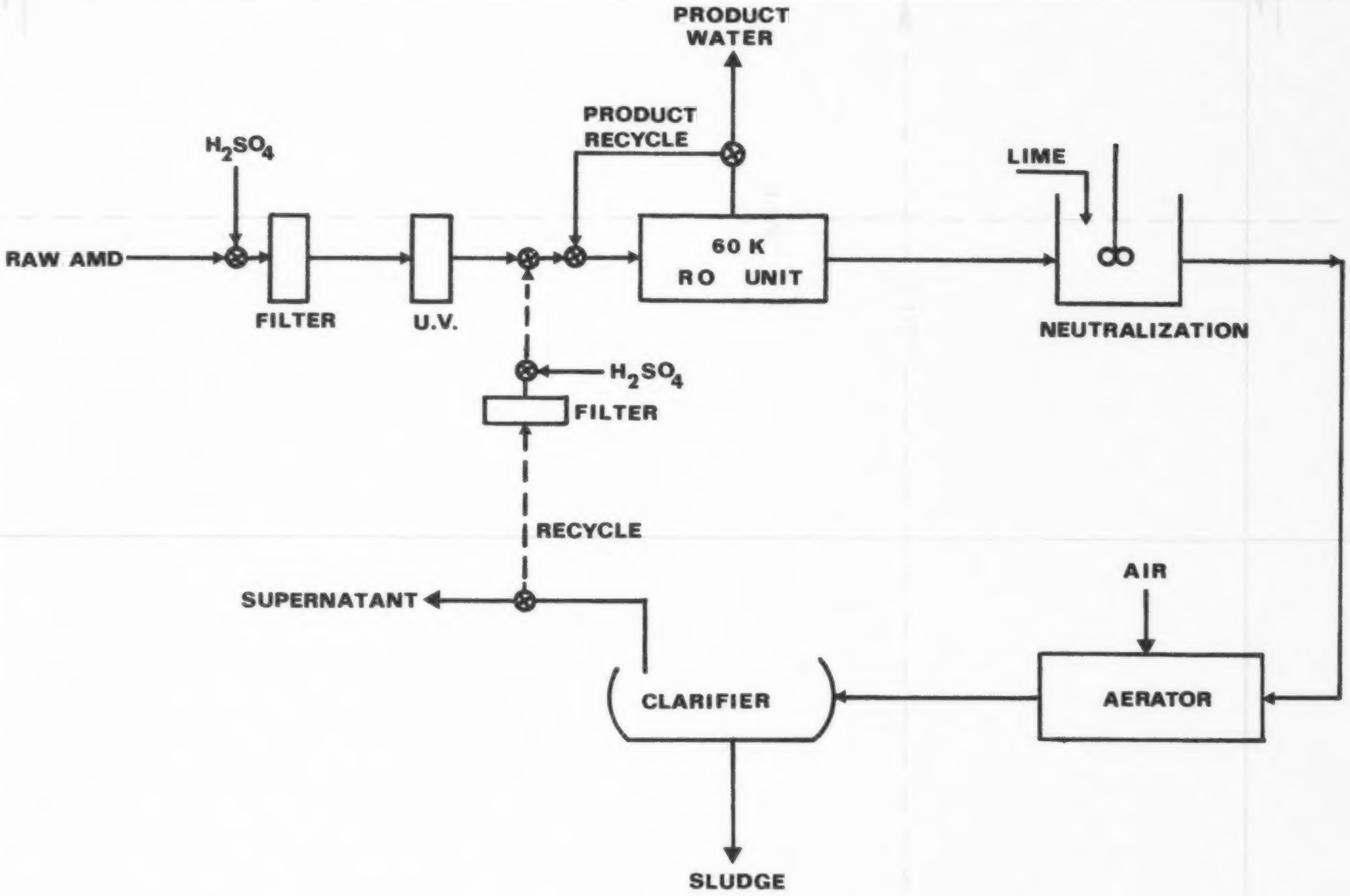
RAW AMD
H_2SO_4
FILTER
U.V.
PRODUCT RECYCLE
PRODUCT WATER
60 K RO UNIT
LIME
NEUTRALIZATION
H_2SO_4
FILTER
RECYCLE
SUPERNATANT
AIR
CLARIFIER
AERATOR
SLUDGE

Figure 26. Process schematic for lime neutrolosis studies.

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Theoretical Evaluation

Rationales to illustrate the advantages of once-through type AMD treatment operations versus neutrolosis processes are presented in Appendix B using Figures B-2 through B-4, which were developed from the models of the neutrolosis process also noted in Appendix B. In particular, Figures B-3 and B-4 show the saturation factor for calcium sulfate in the RO unit brine as a function of overall system product water recovery, with the percentage of brine recycle and the reverse osmosis unit recovery as parameters. The maximum allowable gypsum concentration was empirically determined from observations of the calcium sulfate levels at which the RO unit could operate without noticeable membrane fouling. This corresponded to a saturation factor of 1.4, as determined by the ionic interference computational methods of Appendix B.

There is another primary problem with neutrolosis not readily evident from the models and plots. The tolerable $CaSO_4$ saturation limit, which is used in Figure B-2 (and the zero recycle lines of Figures B-3 and B-4), is applicable to once-through treatment of AMD. However, it is highly doubtful that this limit holds for the neutrolosis process, because the supernatant recycle to the RO unit is supersaturated with calcium sulfate. (For these plots the saturation factor of the supernatant was assumed to be 1.4, and the operating lines will pinch at whatever value of supernatant saturation is specified.) The recycle stream is loaded with precipitate nuclei because it is not practical to provide adequate residence time in the clarifier for the removal of all of the precipitable gypsum. These nuclei are not completely destroyed when the recycle and raw feed streams are mixed because of the finite time required for dissolution. When this blended stream is concentrated to the point where it is supersaturated in calcium sulfate, these remaining nuclei can attach themselves to the membranes and promote precipitation, causing it to occur much more rapidly than in the presence of a 'clean' surface. Because of this effect, the tolerable saturation factor is lowered for the neutrolosis case. This can be demonstrated by writing the precipitation rate as

$$\text{rate} = K(\rho - 1)^n,$$

where K and n are constants, and ρ is the saturation factor. Assume for simplicity that $n = 1$ and that the rate constant K for the neutrolosis case, K_2, is twice that for the once through case, K_1, due to the effect of the entrained nuclei from the recycle stream. For the rates to be equal

$$K_1(\rho_1 - 1) = K_2(\rho_2 - 1),$$

or

$$K_1(\rho_1 - 1) = 2K_1(\rho_2 - 1) .$$

Solving for ρ_2,

$$\rho_2 = (\rho_1 + 1)/2 ,$$

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and if

$$\rho_1 = 1.4,$$

$$\rho_2 = 1.2.$$

Therefore, the tolerable saturation factor is lowered for the case where neutralized supernatant is recycled to the RO unit. Thus, there appears to be no way that the neutrolosis process can be operated as conceived for any length of time before severe membrane fouling commences. In fact, no practical operation is possible at a recovery where the saturation factor is greater than 1.4 for the once-through operation. Below such a recovery level, Appendix B shows that the once-through operation is always better.

Another difficulty which arises is the buildup of sodium sulfate in the recycle loop. This problem was not encountered at the Norton site because the feed water contained no sodium. Due to the extremely high solubility of sodium sulfate at ambient temperatures (200-400 g/liter), sodium sulfate will build up in the recycle loop until its saturation limit is reached. Since neutralization has no effect on the sodium sulfate, the resulting high sodium concentration in the process loop will cause deteriorated product water quality due to sodium ion leakage. Excessive buildup of sodium sulfate also will cause a substantial increase in the osmotic pressure of the brine. In fact, the resulting osmotic pressure might be so high (greater than 1,380 kN/m^2, 200 psi) that it would be difficult to maintain an acceptable product water flux without operating the RO unit at extremely high feed pressures (approaching 6,900 kN/m^2, 1,000 psi). These high pressures would tend to reduce membrane life, thus increasing maintenance problems and costs. The only alternative is to 'bleed off' a certain amount of the concentrated brine in order to prevent accumulation of sodium sulfate, therefore negating the advantage of having only the product water and a low volume sludge as exiting streams from the process.

In summary, the following conclusions seem evident:

- Even if ideal calcium sulfate saturation conditions are achieved in the neutralization and clarification procedures, neutrolosis processes provide no advantage over RO treatment operations on a once-through recovery basis.

- In practice, $CaSO_4$ equilibrium in the brine is not attained, and gypsum precipitation occurs at the surfaces of filters and membranes which act as crystal formation sites. This is totally undesirable for establishing long-term, low-maintenance operations. In fact, any neutrolosis process would probably have to operate at points well-below the 1.4 $CaSO_4$ brine saturation factor line, which is the limiting case in this study.

- The pumping costs for neutrolosis will always be greater than for a once-through RO system operation for a specified product flow rate.

EPA-287 (Cin.)
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TYPING GUIDE SHEET

- The neutrolosis process will feature a continuous building up to solubility limits of normally soluble constituents in the neutralized brine in the clarifier, e.g. sodium sulfate. The $CaSO_4$ saturation effect happens to occur immediately; however, if this could be hypothetically overcome, other compounds would reach their saturation levels over a longer period of time during the neutrolosis mode of operation. Computations would show this, with such phenomena acting as a deterrent to other forms of neutrolosis, such as soda ash neutralization or lime-soda softening techniques.

- Although refinements could be incorporated into the models and computations used to generate the information presented in Appendix B, it is believed that neutrolosis cannot be as successful as a once-through recovery type operation. Neutrolosis may be sustained for a short period of several hours at or above $CaSO_4$ saturation levels; however, fouling rapidly establishes itself, and the system cannot be operated at conditions over the long term which can be technically or economically justified.

Experimental Studies

Although relatively simple theoretical models pointed to several negative conclusions regarding neutrolosis using lime as the neutralizing agent, it was necessary to present experimental evidence to support these assertions.

The first series of experiments conducted was a set of preliminary runs to evaluate the lime neutralization/aerator/clarifier process train, and to determine whether the resulting clarified effluent was suitable for recycle to the reverse osmosis unit. During these experiments, the system was operated in the open-loop configuration. Figure 26 (without the dashed recycle line) depicts the experimental arrangement. The 60K RO unit was operated at 50, 60, and 75 percent unit recovery levels which produced brine flow rates of 2.65 lps, 1.77 lps, and 0.88 lps (42 gpm, 18 gpm, and 14 gpm), respectively.

It was noted throughout the course of these operations that poor sludge settling occurred in the clarifier. It was never possible to obtain an effluent turbidity of less than 40 Jackson Turbidity Units (JTU) during these operations, a turbidity level believed to be much too high to permit the supernatant to be recycled to the RO unit. Another observation was that most of the iron was converted to the ferric state in the lime reactor.

These results led to several modifications in the operation of the system. Due to the high iron conversion in the lime reactor, and because it was felt that the turbulence in the aerator was breaking up the flocculent, a decision was made to operate the system without the aeration step. It was also decided to operate the clarifier with intermittent rake operation and periodic sludge removal in hopes that sludge settling in the

EPA-287 (Cin.)
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clarifier could be improved. A 146.4-hour run at 75-percent unit recovery was performed with these system modifications, during which the following conditions were maintained:

Raw AMD feed flow rate	1.67 lps (26.5 gpm)
Product blend flow rate	1.86 lps (29.5 gpm)
Blended flow rate	3.53 lps (56.0 gpm)
Product flow rate	2.65 lps (42.0 gpm)
Brine flow rate	0.88 lps (14.0 gpm)
Brine conductivity	7,000 μmhos/cm
Clarifier underflow rate	0.19 lps (3.0 gpm)
Neutralized brine pH	7.5 - 8.0
Clarifier supernatant pH	8.0
Clarifier supernatant turbidity	40-50 JTU

In the course of this operation, some critical problems were still encountered. One major difficulty was obtaining a well-clarified supernatant. The turbidity of the supernatant was much too high to permit recycle through 10-micron filters preceding the RO unit. In order to affect some solution, it was decided to explore whether injection of 1.5-2.5 mg/l levels of Dowell M-144 and M-924 anionic and cationic flocculating agents into the neutralized brine stream would help improve the sludge settling. These additives did help reduce the supernatant turbidity to the 20-25 JTU level. However, even when this supernatant was recycled, the 10-micron filters became plugged very rapidly. At this stage, it was determined that most of the turbidity and fouling of the filters was due to calcium sulfate precipitation.

This continual gypsum formation posed the most frustrating problem. Due to the supersaturation of the clarifier supernatant, calcium sulfate precipitate was constantly being produced. TABLE 7 presents the results of the chemistry analysis of the process streams involved. Using this chemistry data and the ionic interference method for calculating the saturation factor, it was determined that the 60K RO systems brine had a saturation factor of 1.31, while the supernatant had a saturation factor of 1.73 (where a factor of 1.0 indicates that the solution is saturated). Thus, with respect to calcium sulfate formation, the supernatant was not suitable for recycle to the RO unit.

Another problem noted at this time was that calcium sulfate precipitation was further promoted when the recycle stream was acidified with sulfuric acid. It was concluded that the additional sulfate ion was responsible for this. This problem did not occur when phosphoric acid was used, but the use of phosphoric acid entailed addition of another pollutant to wastewaters. Muriatic acid also should have been tried, but was not.

Test results with the open loop system indicated that conclusions drawn previously about the quality of the supernatant with respect to calcium sulfate were correct. The recycle stream was highly saturated with calcium sulfate, and gypsum precipitated very rapidly when suitable surfaces were contacted, such as filter and membrane surfaces.

EPA-287 (Cin.)
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TABLE 7. CHEMISTRY ANALYSIS FOR LIME NEUTRALIZATION OF 60K RO UNIT BRINE AT 75-PERCENT UNIT RECOVERY

	Raw Feed	Blended Feed	Brine	Product	Supernatant from Clarifier
Conductivity, µmhos/cm	4000	2600	8000	45	6200
pH	4.5	2.7	2.4	4.2	7.6
Acidity (as $CaCO_3$ to end point pH 7.3), mg/l	720	520	1700	95	--
Ca, mg/l	450	160	640	0.97	1200
Mg, mg/l	150	58	220	0.36	190
Total Fe, mg/l	330	140	520	0.80	0.80
Fe^{2+}, mg/l	310	130	490	<0.80	<0.80
Na, mg/l	470	210	570	3.0	270
Al, mg/l	6.3	4.1	8.0	0.09	6.2
Mn, mg/l	5.2	3.9	6.8	0.07	5.2
SO_4, mg/l	3300	1300	5600	16	5000
TDS, mg/l	4700	1900	7600	21	6600

In order to examine the performance of an RO system when an actual lime neutrolosis recycle operation occurs, several experimental runs were conducted. The calcium sulfate brine saturation factor was selected as a significant variable, since its limiting value of 1.4 (based on ionic interference solubility calculations) appeared widely applicable to the RO treatment of a diversity of AMD feeds. In an evaluation of RO systems operation, it is the fouling potential of the brine in the last bank of modules which is of critical importance. For Crown AMD, the 1.4 calcium sulfate saturation factor represented Ca^{++} concentrations of 750-800 mg/l in the brine stream. It should further be noted that based on non-ionic interference calculations (comparison of solubilities of $CaSO_4$ in brine with $CaSO_4$ solubility in distilled H_2O), the 1.4 value cited above corresponded to a non-ionic interference $CaSO_4$ saturation factor of 2.45.

One experimental investigation of lime-based neutrolosis was conducted using an acidified tap water raw feed to the 60K RO unit, with the waste brine neutralized to pH 11.0. Run conditions were as follows:

Tap water flow rate	0.38 lps	(6 gpm)
Product flow rate	2.52 lps	(40 gpm)
Brine flow rate	0.38 lps	(6 gpm)
Supernatant recycle flow rate	0.25 lps	(4 gpm)
Brine to waste flow rate	0.13 lps	(2 gpm)
Product recycle flow rate	2.27 lps	(36 gpm)
Blended feed flow rate	2.70 lps	(46 gpm)
Product flow rate from system	0.25 lps	(4 gpm)
Unit Recovery	87.0%	
Overall Systems Recovery	66.7%	

Two representative chemistry analyses taken during this one week operation are given in TABLES 8 and 9, with the time-dependent product flux (log-log slope ≈-0.03) in the last tube bank of the 5-4-2-2-1 array shown in Figure 27. Note the apparent buildup of sodium and sulfates in the brine and supernatant over the two-day period. Although flux decline could not be totally attributed to fouling at brine $CaSO_4$ saturation factors of 1.06-1.08, the neutrolosis process was not really effective on this very weak feed, since with proper design of a once-through recovery RO system, the tap water recovery could have theoretically exceeded 95 percent.

Thus, the "tap water neutrolosis" study again provided evidence that the lime neutrolosis mode of operation is not comparable to a once-through recovery process. Operational problems also were encountered with respect to increased acid consumption for feed pH adjustment of the blended feed to the RO unit, and more frequent replacement of cartridge filters was due to the precipitation of gypsum present in the supernatant. These problems had been anticipated; and, in fact, proved to be recurrent in all lime neutrolosis schemes attempted.

Another neutrolosis operation at pH 8 and 50-percent supernatant recycle was conducted with Crown AMD in order to determine how well the RO system could perform with a more severely concentrated feed. TABLE 10 contains the pertinent chemistry and operational data. From the information in TABLE 10, with a supernatant saturation factor of 1.42 and pH 8, the results of a theoretical analysis of Crown feed with brine neutralization to pH 8 could be compared to the observed results. For a 50-percent supernatant recycle and an overall recovery of 57 percent, Appendix B methods yield a theoretical brine saturation factor of 1.5, compared to 1.65 calculated from the actual data. There were a number of experimental errors in the observed results which could account for this. Small errors in flow rate measurements and chemistry analyses could explain a 10-percent difference, particularly when coupled with any non-equilibrium phenomena. In this light, the agreement was at least "fair" between theory and experiment.

The most significant factor of this study was that both theory and experimentally observed data indicated that severe membrane fouling should occur in the last bank of the 5-4-2-2-1 array. Figure 28 shows that this was indeed the case; and, in fact, the fouling caused a flux decrease of 15 percent within one day after the initiation of the neutrolosis operation (which followed a five-day membrane compaction period).

In summary, the lime-based neutrolosis process caused an intolerable membrane fouling rate when attempting to sustain a long-term, high overall RO system recovery operation. Although numerous attempts were made to run lime neutrolosis experiments, all were rather short-lived and unsuccessful due to prefiltration system fouling and/or deterioration of product water flux rates, even when precipitate inhibitors such as those discussed in SECTION 6 were introduced to the process.

TABLE 8. CHEMISTRY ANALYSIS FOR TAP WATER LIME NEUTROLOSIS STUDY (pH 11) - DAY 2

	Tap Water	Brine	Supernatant
Ca, mg/l	10	560	740
Mg, mg/l	2.2	18	18
Total Fe, mg/l	0.04	0.62	0.12
Na, mg/l	10	130	85
Al, mg/l	1.2	1.3	0.6
Mn, mg/l	0.01	0.01	0.01
SO_4, mg/l	79	1900	2200
$CaSO_4$ Saturation Factor	---	1.06	1.23

TABLE 9. CHEMISTRY ANALYSIS FOR TAP WATER LIME NEUTROLOSIS STUDY (pH 11) - DAY 4

	Tap Water	Brine	Supernatant
Ca, mg/l	12	570	840
Mg, mg/l	2.0	15	19
Total Fe, mg/l	<0.01	0.46	0.20
Na, mg/l	15	230	190
Al, mg/l	0.75	0.86	1.1
Mn, mg/l	0.01	0.04	0.07
SO_4, mg/l	---	2000	2500
$CaSO_4$ Saturation Factor	---	1.08	1.33

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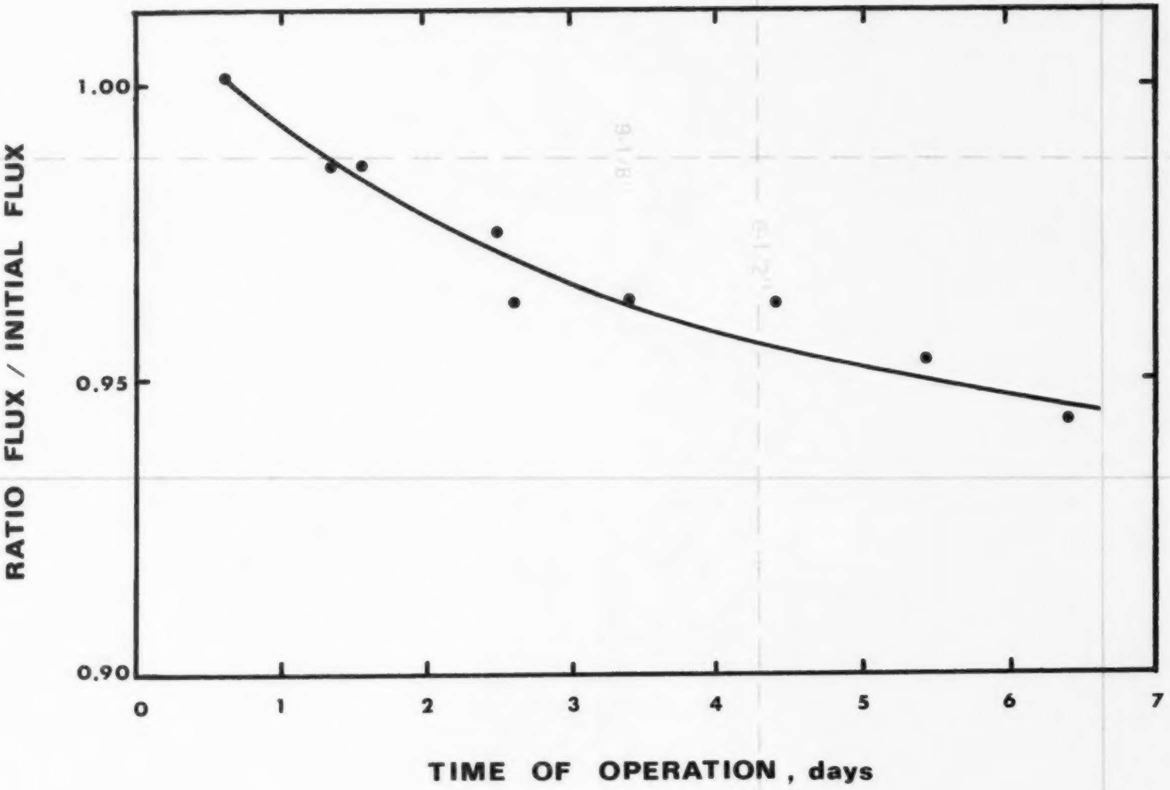

Figure 27. 60K RO unit product flux in last tube bank for tap water neutrolosis study at pH 11.

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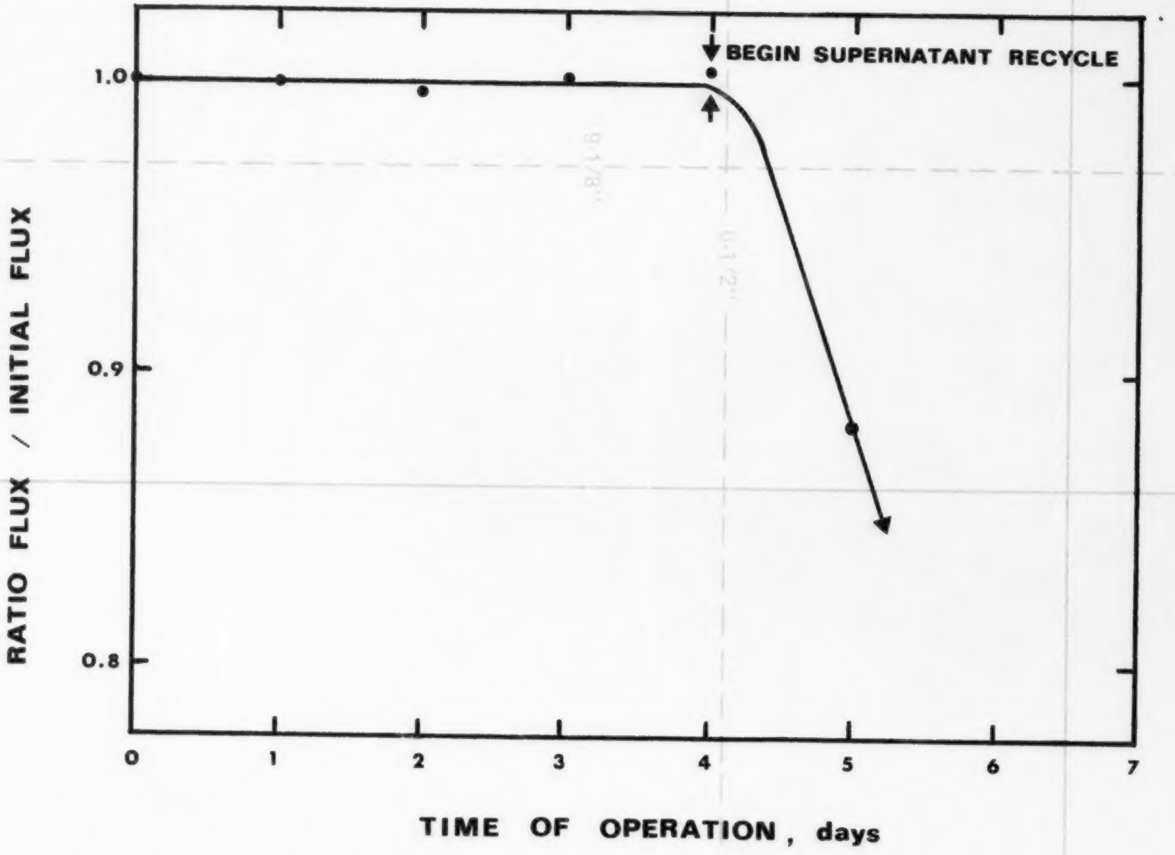

Figure 28. 60K RO unit product flux in last tube bank for Crown AMD lime neutrolosis study at pH 8.

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TABLE 10. CHEMISTRY AND OPERATIONAL DATA: CROWN AMD LIME NEUTROLOSIS STUDY (pH 8)

	Feed	Brine	Supernatant
Ca, mg/l	320	910	780
Mg, mg/l	120	150	50
Total Fe, mg/l	330	300	1.6
Fe^{2+}, mg/l	330	--	--
Na, mg/l	380	890	480
Mn, mg/l	6.8	8.0	0.86
Al, mg/l	35	36	2.0
SO_4, mg/l	2700	7100	4100
$CaSO_4$ Saturation Factor	--	1.65	1.42

Raw AMD feed flow rate - 0.44 lps (7.0 gpm)
Product flow rate - 2.52 lps (40.0 gpm)
Product recycle flow rate - 2.27 lps (36.0 gpm)
Product flow rate from system - 0.25 lps (4.0 gpm)
Blended feed flow rate - 2.90 lps (46.0 gpm)
Brine flow rate - 0.38 lps (6.0 gpm)
Supernatant recycle flow rate - 0.19 lps (3.0 gpm)
Brine to waste flow rate - 0.19 lps (3.0 gpm)
Overall systems recovery - 57.1%
Unit recovery - 90.0%

SODA ASH NEUTROLOSIS

Because of the gypsum fouling which resulted from lime neutrolosis, it was decided to attempt operations using soda ash (sodium carbonate) as the neutralization agent in place of the lime. It was expected that calcium sulfate hardness could be removed with the soda ash and thus circumvent the principal difficulty which was associated with lime neutrolosis. Operating experience with soda ash neutralization of AMD has been reported by Tarpley (25), and by Wilmoth and Hill (21), who noted that soda ash was a very effective neutralizing agent, but that its cost was prohibitive compared to lime and limestone.

Basic Principles

Soda ash (Na_2CO_3) is used to raise the pH of the water and thus acts to precipitate the metals as insoluble hydroxides. As discussed in the section on lime neutrolosis, the pH is controlled to remove most of the various metals present. Addition of soda ash to proper pH levels allows the iron, manganese, aluminum, and magnesium to be removed to the same extent as with the lime process. The great differences between the two processes have to do with the hardness removal and cost.

The chemical reactions which take place are as follows:

$$\text{A)}\quad Na_2CO_3 \rightarrow 2Na^+ + CO_3^=,$$

$$\text{B)}\quad 2(H^+\cdot OH^-) + CO_3^= \rightarrow H_2CO_3 + 2OH^-,$$

$$\text{C)}\quad H_2CO_3 \rightarrow H_2O + CO_2\uparrow,$$

$$\text{D)}\quad (M^z)_a(SO_4)_b + 2b(Na)^+ + az(OH)^- \rightarrow aM(OH)_z\downarrow + bNa_2SO_4,$$

plus the calcium sulfate hardness removal reaction

$$\text{E)}\quad CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4$$

It can be seen that this reaction scheme possesses the advantage of being able to remove calcium sulfate. The countering disadvantage is that insoluble calcium carbonate is formed. This product will saturate the supernatant, but it is not known how serious the fouling in the RO unit would be due to calcium carbonate. It must be noted that the high sulfate concentration in the supernatant arising from the sodium sulfate could present potential calcium sulfate fouling problems when mixed with raw AMD, due to the sulfate shifting the solubility equilibrium.

Another significant factor is that efficient removal of carbon dioxide is important, both to insure the completion of the metal removal reactions and to make the most effective use of the soda ash. This should pose no serious problem provided that adequate agitation, residence time, and surface exposure are provided during the course of the reaction. (One place where the carbon dioxide did prove troublesome in practice was when supernatant was mixed with raw feed and acidified with sulfuric acid, causing evolution of CO_2 via the $[H_2SO_4 + CaCO_3 \rightarrow CO_2 + H_2O + CaSO_4]$ reaction. However, it was not determined whether the presence of this CO_2 had any deleterious effect on the operation of the RO unit, or the membranes themselves.)

The reactions which precipitate the metals all produce sodium sulfate as a product. Thus, the buildup of sodium sulfate is inevitable in such a neutrolosis type recycle system. High osmotic pressure, deteriorated product water quality, and possible fouling due to calcium carbonate are some of the consequences of such a concentration of sodium sulfate in the process loop. Although no fouling problem should be encountered unless very high system recoveries are involved, the other problems are significant. If high quality product water is required, the resultant sodium sulfate concentration might well be unacceptable. The elevated osmotic pressure would require high feed pressure operation in order to provide a sufficient driving force to maintain an adequate product flux. Low flux means a large membrane area to provide the required product rate, which entails a large investment in membranes. Alternatively, a high operating pressure can lead to a shortened membrane life and increased replacement cost. The system would either require some method of 'bleed-off' in order to maintain the sodium sulfate concentration at a moderate level, or else these undesirable effects would have to be tolerated.

In addition, a considerable amount of soda ash would be required for all but the most dilute feeds in order to affect the removal of all but sodium metal ions in the neutralization process. With the price of soda ash a factor of five to ten greater than lime, this would certainly pose an economic disadvantage towards serious consideration of soda ash neutralization or neutrolosis systems. Preliminary indications are that the chemical costs would exceed $2.00 per 3,790 l (1,000 gal) of treated Crown AMD, a fact that might well rule out soda ash as a neutralization candidate for Crown AMD.

Experimental Studies

Although the preliminary evidence indicated that soda ash neutrolosis might not be a practical candidate for treatment of Crown AMD, it was believed that certain investigations were in order to study some operational aspects of the process. These were conducted in two parts:

1. An "open loop" process in which a blended AMD feed was first treated by the 60K RO unit at 75-percent unit recovery, with 0.29 lps (4.6 gpm) of neutralized supernatant resulting from 60K RO unit treatment blended with 0.16 lps (2.6 gpm) of raw AMD and treated by the 4K RO unit, followed by 4K RO treatment of supernatant only. The process flowsheet is shown in Figure 29.

2. A "closed loop" conventional neutrolosis process in which the 60K RO unit was operated at 90 percent unit recovery with 0.2 lps (3.1 gpm) of soda ash neutralized brine recycled to the system. The process flow sheet for this operation is similar to that of Figure 26 for the lime neutrolosis case.

The "open loop" run lasted 18 hours and consisted of two stages: a 14-hour run using blended AMD and 60K RO supernatant as feed to the 4K RO unit, followed by an immediate switch to a "supernatant only" feed to the 4K RO system for the final 4 hours. The use of 1 mg/l each of anionic and cationic flocculents, coupled with a residence time of 10-12 hours in the clarifier, had reduced the pH 9.0 supernatant turbidity to 7 JTU, which was quite satisfactory for recycle operations.

The chemistry data for the "open loop" study are presented in TABLES 11 and 12, and the product flows in the 4K RO unit are shown in Figure 30. Examination of the 60K RO brine and the neutralized clarifier supernatant shows that only the iron, aluminum, and manganese were removed to any degree by the neutralization procedure. The magnesium and calcium were comparatively unaffected. In fact the failure to remove $CaSO_4$ from the brine directly contributed to the rapid flux decline in the 4K RO unit when it was operated on supernatant feed only (Figure 30).

Although an insufficient amount of soda ash had been added to cause calcium and magnesium hardness removal, it can be seen that the amount of sodium in the clarifier supernatant was double that present in the 60K RO

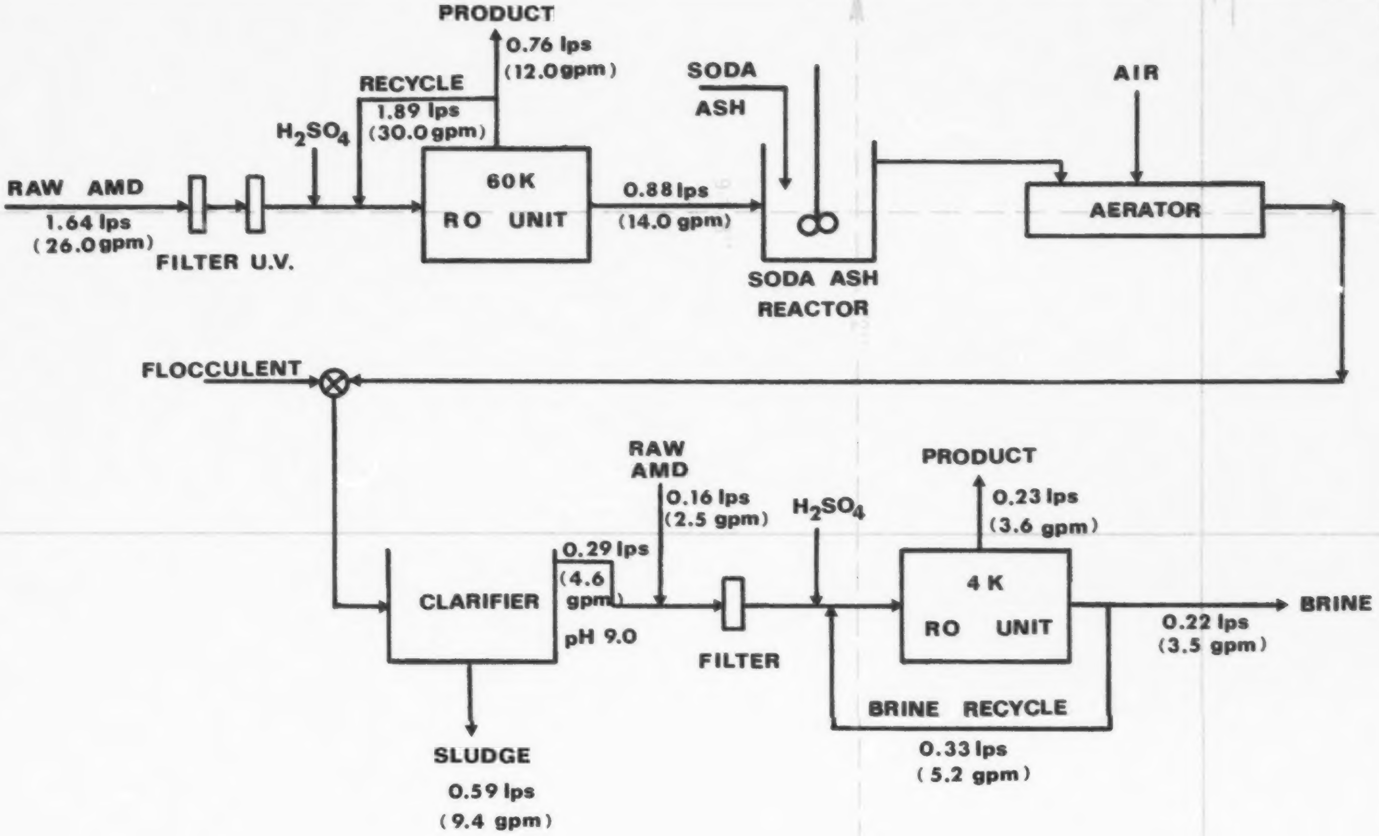
PRODUCT
0.76 lps
(12.0gpm)
RECYCLE
1.89 lps
(30.0gpm)
H_2SO_4
RAW AMD
1.64 lps
(26.0gpm)
FILTER U.V.
60K
RO UNIT
0.88 lps
(14.0 gpm)
SODA
ASH
SODA ASH
REACTOR
AIR
AERATOR
FLOCCULENT
RAW
AMD
0.16 lps
(2.5 gpm)
H_2SO_4
PRODUCT
0.23 lps
(3.6 gpm)
CLARIFIER
0.29 lps
(4.6
gpm)
pH 9.0
FILTER
4 K
RO UNIT
BRINE
0.22 lps
(3.5 gpm)
BRINE RECYCLE
0.33 lps
(5.2 gpm)
SLUDGE
0.59 lps
(9.4 gpm)

Figure 29. Flowsheet for "open loop" soda ash neutrolosis study.

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TABLE 11. CHEMISTRY ANALYSIS FOR "OPEN LOOP" STUDY, HOURS 1-14, (BLENDED RAW AMD AND SUPERNATANT FEED)

	Raw Feed	60K Brine	60K Product	Clarifier Supernatant	4K Brine	4K Product
Ca, mg/l	330	510	1.2	580	590	2.8
Mg, mg/l	48	180	0.51	210	240	1.0
Total Fe, mg/l	230	400	1.2	0.26	130	0.60
Fe^{+2}, mg/l	220	370	<1.2	<0.26	120	<0.60
Na, mg/l	650	1100	4.6	2500	2600	38
Al, mg/l	1.70	4.2	0	0.21	1.4	0.11
Mn, mg/l	4.8	7.4	0.04	5.5	6.0	0.04
SO_4, mg/l	3200	5200	20	6000	8300	--
pH	4.5	2.1	--	9.0	--	--

TABLE 12. CHEMISTRY ANALYSIS FOR "OPEN LOOP" STUDY, HOURS 14-18, (SUPERNATANT FEED ONLY)

	Raw Feed	60K Brine	Clarifier Supernatant	4K Brine
Ca, mg/l	330	760	810	1200
Mg, mg/l	48	190	220	730
Total Fe, mg/l	230	600	4.6	22
Fe^{+2}, mg/l	220	540	--	21
Na, mg/l	650	1000	2000	6300
Al, mg/l	1.7	1.8	0.85	1.1
Mn, mg/l	4.8	9.8	5.6	26
SO_4, mg/l	3200	6200	6100	15000
pH	4.4	2.1	8.9	--

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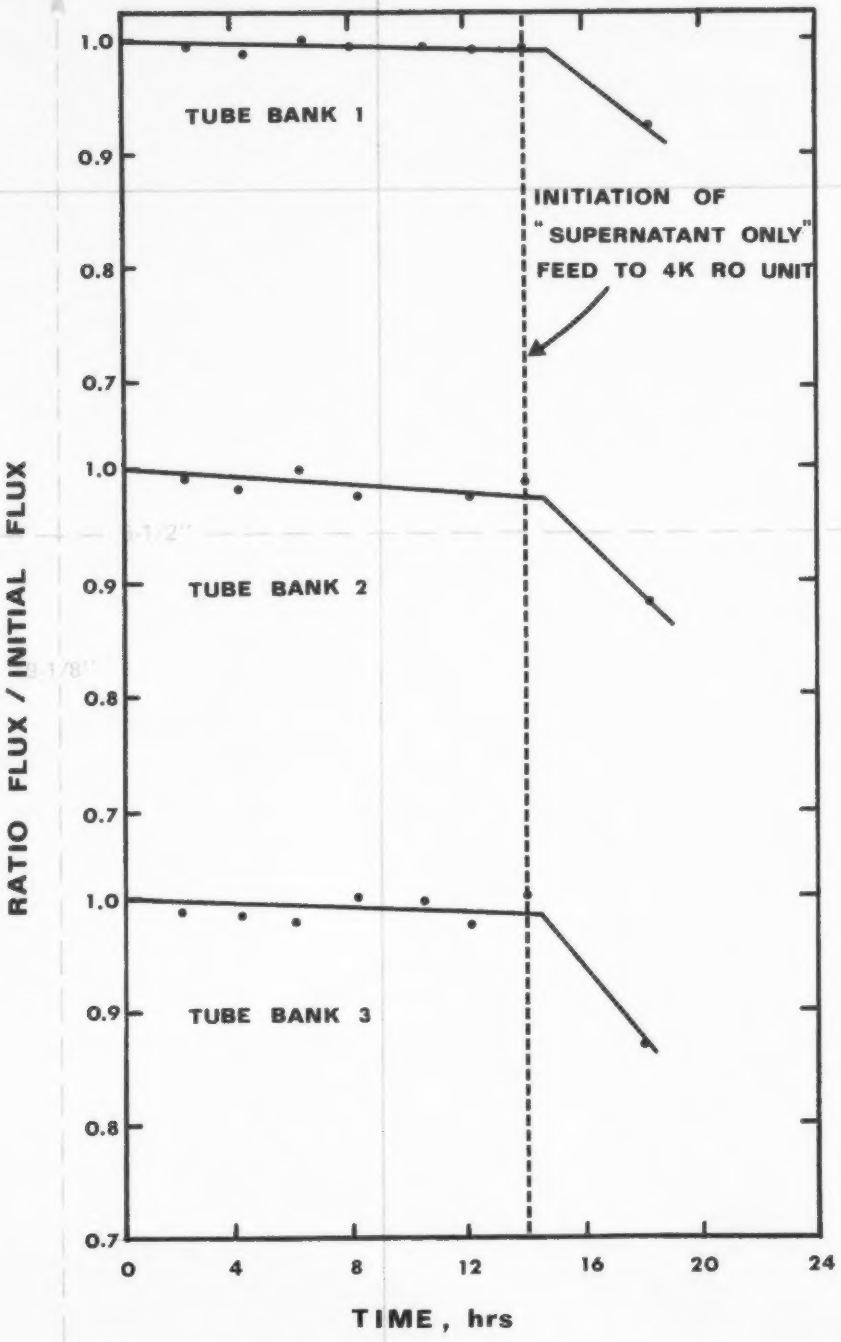

Figure 30. 4K RO unit product fluxes for "open loop" soda ash neutrolosis study.

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unit brine. This did nothing to alleviate $CaSO_4$ fouling potential, but did result in an increased osmotic pressure of the feed to the RO unit, and of course increased levels of sodium in the product water.

Additional bench-scale neutralization tests on Crown AMD indicated that soda ash neutralization of the RO brine to a pH level of greater than 9.5 would be capable of removing 90 percent of the calcium hardness. This was the neutralization bench mark pH value for the "closed loop" experiment which followed, using the 60K RO unit. The run conditions during the four day operating period were:

Raw AMD feed flow rate	-	.47 lps	(7.4 gpm)
Blended feed flow rate	-	2.90 lps	(46.0 gpm)
Product flow rate	-	2.65 lps	(42.0 gpm)
Product flow rate from system	-	.41 lps	(6.5 gpm)
Total brine flow rate	-	.25 lps	(4.0 gpm)
Brine flow rate to waste	-	.06 lps	(0.9 gpm)
Supernatant recycle flow rate	-	0.20 lps	(3.1 gpm)
Product recycle flow rate	-	2.24 lps	(35.5 gpm)
Unit recovery	-	91.3%	
Overall system recovery	-	87.8%	
Supernatant pH	-	9.6	

Chemistry analyses for each day of the four-day operation are shown in TABLE 13. It can be seen that for a supernatant pH of 9.6, the calcium removal was better than 95 percent; however, the Na_2SO_4 buildup in the supernatant increased ten-fold during the operating period. This verified the hypothesis that increased sodium concentrations in the soda ash neutrolosis mode of operation will occur.

Examination of Figure 31 shows that the product flux indeed declined in the last bank of the 5-4-2-2-1 pressure vessel array used for 90-percent recovery operations. This deterioration of product flux was attributed to increased osmotic pressure resulting from continuing sodium ion concentration buildup in the supernatant. Verification of this occurred when the supernatant recycle was terminated and replaced by an equivalent amount [0.2 lps (3.1 gpm)] of raw AMD, resulting in immediate product flux restoration at the same tube bank pressure.

An evaluation of soda ash consumption during the "closed loop" operation indicated that the neutralization chemical costs themselves were greater than \$2.00 per 3,790 l (1,000 gal) of treated AMD, which supported the earlier contention that soda ash neutrolosis (at least from Crown AMD) would be an expensive process.

COMBINED LIME-SODA ASH NEUTROLOSIS

The lack of operational success of lime neutrolosis and the high cost of soda ash neutrolosis led to a brief preliminary examination of a lime-soda ash neutrolosis process, whereby waste brine from the RO unit was neutralized to pH 8.0 with lime, and then raised to pH 10.0 by further

TABLE 13. CHEMISTRY ANALYSIS FOR "CLOSED LOOP" SODA ASH NEUTROLOSIS (ALL CONCENTRATIONS IN mg/l)

	Ca	Mg	Total Fe	Fe^{+2}	Na	Al	Mn	SO_4
DAY 1								
Brine	470	140	230	220	2700	9.2	5.7	8900
Supernatant	17	95	0.7	0	1500	2.2	0.14	6000
Product	0.35	0.2	0.3	<1.0	14	1.0	<0.01	46
DAY 2								
Brine	420	230	230	230	3400	8.6	5.6	11000
Supernatant	16	140	6	0	3000	2.2	0.16	7200
Product	0.65	0.3	0.5	<2.9	20	0.6	<0.01	48
DAY 3								
Brine	450	230	240	200	3500	5.6	4.4	11000
Supernatant	18	150	2.20	0	12000	3.2	0.17	
Product	0.66	0.37	0.32	<2.9	32	0.6	<0.01	74
DAY 4								
Brine	470	210	350	270	10000	10.0	6.2	
Supernatant	17	160	2.2	0	17000	2.2	0.26	
Product	0.60	0.34	0.6	<1.0	50	1.0	<0.01	112

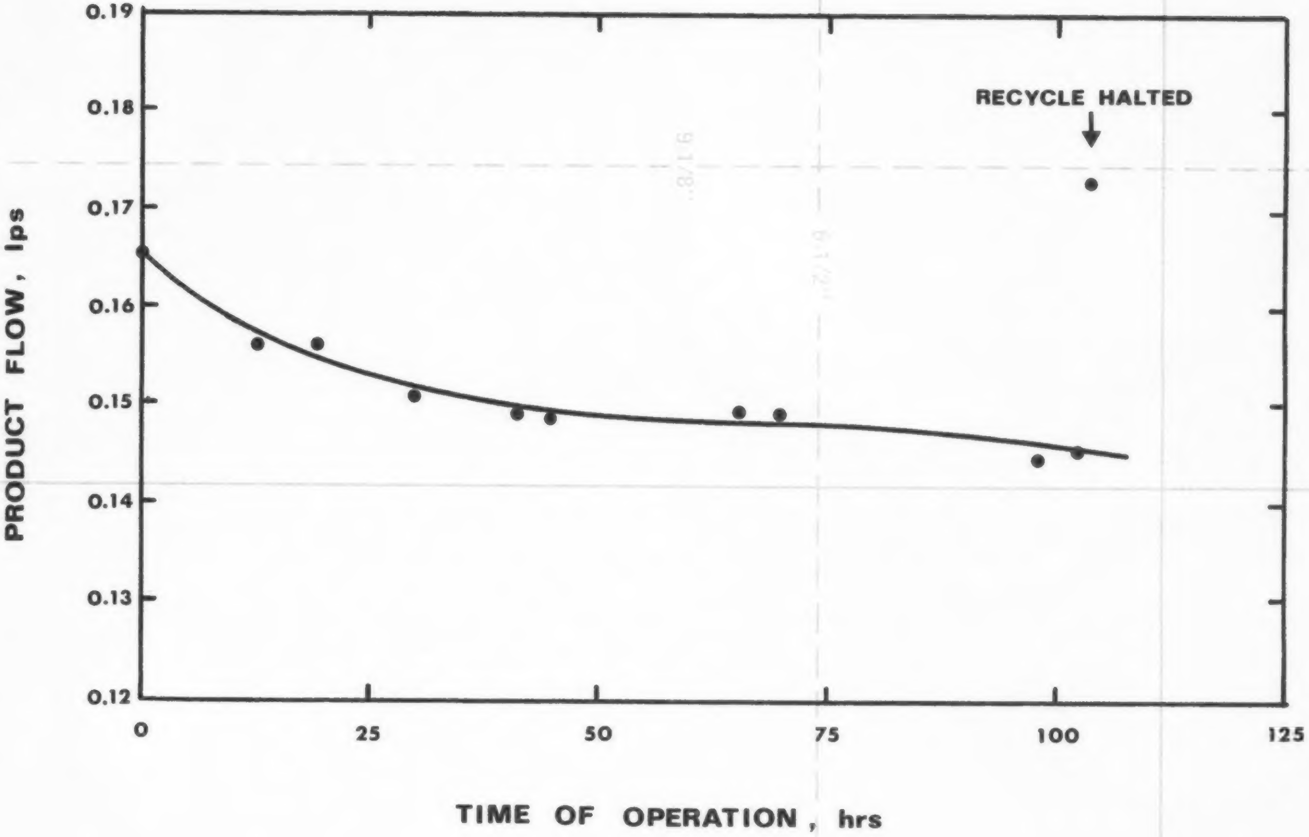

Figure 31. 60K RO unit product flux in last tube bank for "closed loop" soda ash neutrolosis study.

addition of soda ash. These pH values were established by bench-scale experiments conducted with Crown AMD RO waste brine, with the objective being removal of at least 90 percent of the calcium from the supernatant.

The basic chemical reactions which would be involved in lime-soda ash neutralization have already been discussed. In this type of process the concentrate is first lime-treated to remove many of the metals with the cheaper lime. The more expensive soda ash is then added to remove the residual calcium as calcium carbonate, where the goal is to take advantage of the best features of the two neutralization agents. Lime-soda ash treatment has been utilized extensively for the treatment of both industrial water and drinking water (26, 27). However, application to AMD treatment is very recent, and there have been no other reported studies of a neutrolosis type process which utilizes both lime and soda ash.

A 35-hour "open loop" type neutrolosis study was conducted using the lime-soda ash neutralization procedure to pH 10. The process flow sheet is shown in Figure 32. Brine retention time in the lime reactor was eight minutes, and in the soda ash reactor 25 minutes. The lime-soda ash softened brine was then injected with 1 mg/l each of cationic and anionic flocculent (chosen on the basis of previous laboratory tests), and clarified to generate a low turbidity (6-8 JTU) supernatant.

Chemistry data indicated the calcium removal was greater than 90 percent in the 60K RO waste brine; however, there was a continuous flux decline in the 4K RO unit which was treating the supernatant (Figure 33). There was some uncertainty regarding the cause of this decline due to the short duration of the run. However, it seemed unlikely that an osmotic pressure increase due to sodium sulfate buildup would generate the magnitude of flux decline which was observed (log-log slope ≈ -0.05 in tube bank 3). One suspected cause was membrane fouling by calcium carbonate because of its extremely low solubility. The acidification in this experimental arrangement did not remove the carbonate ion, since no provision had been made to release the carbon dioxide which would be generated. If lime-soda ash neutrolosis is to be investigated further, $CaCO_3$ fouling potential must be carefully evaluated.

Lime and soda ash consumption during the study was calculated to cost approximately \$1.50 per 3,790 l (1,000 gal) of Crown AMD waters treated. Although less than soda ash neutrolosis itself, it is still quite costly. Again, the economics of the situation need to be evaluated before any decision is made to promote lime-soda ash neutrolosis as a cost-effective technology. In any neutrolosis process, there will be added equipment costs and involved operational and control procedures which must be carefully monitored, e.g. accurate pH control in neutralization procedures and maintenance of low turbidity conditions in supernatant effluents from clarifiers.

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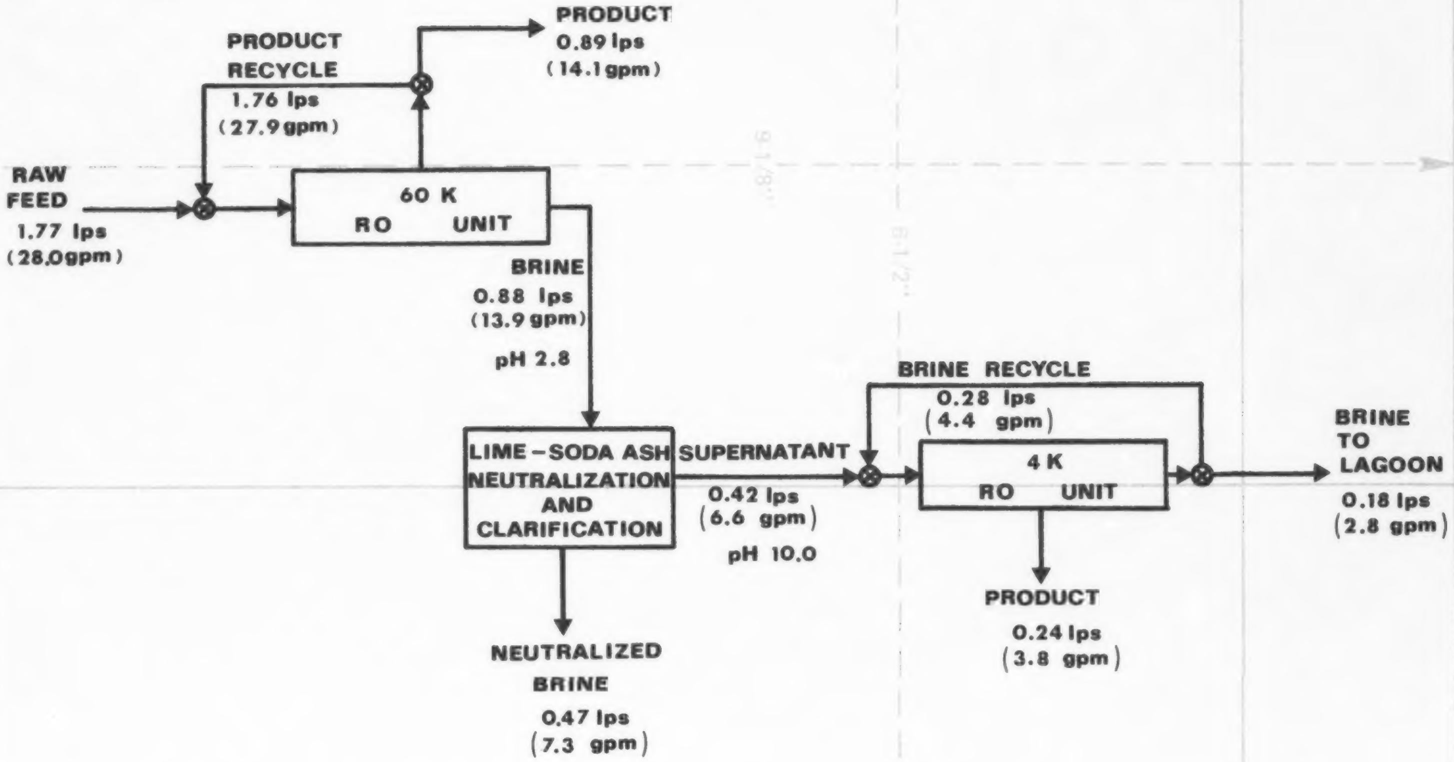
RAW FEED
1.77 lps
(28.0gpm)
PRODUCT RECYCLE
1.76 lps
(27.9gpm)
60 K
RO UNIT
PRODUCT
0.89 lps
(14.1gpm)
BRINE
0.88 lps
(13.9gpm)
pH 2.8
LIME-SODA ASH NEUTRALIZATION AND CLARIFICATION
NEUTRALIZED BRINE
0.47 lps
(7.3 gpm)
SUPERNATANT
0.42 lps
(6.6 gpm)
pH 10.0
BRINE RECYCLE
0.28 lps
(4.4 gpm)
4 K
RO UNIT
PRODUCT
0.24 lps
(3.8 gpm)
BRINE TO LAGOON
0.18 lps
(2.8 gpm)

Figure 32. Flowsheet for "open loop" lime-soda ash neutrolosis study.

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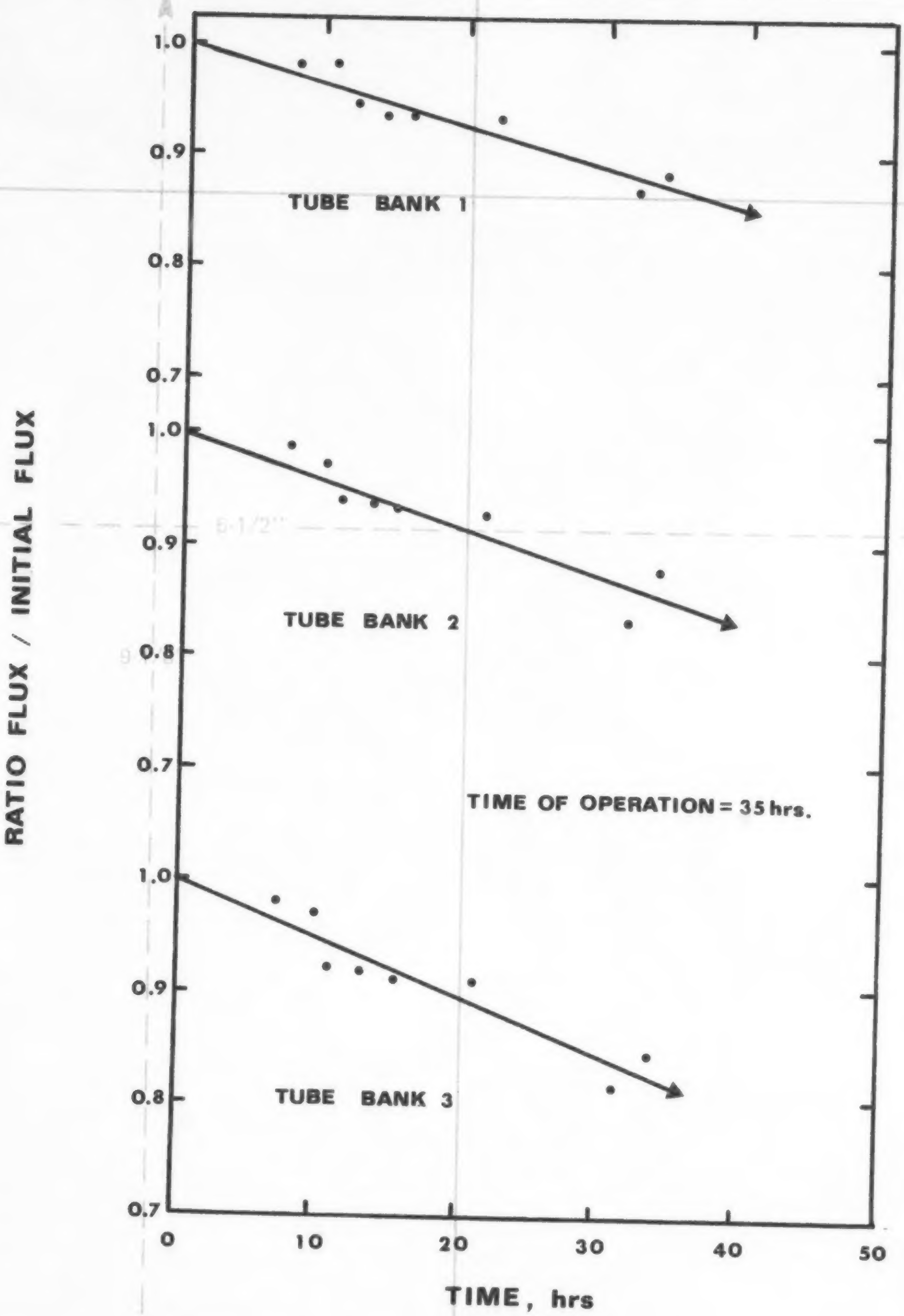

Figure 33. 4K RO unit product fluxes for "open loop" lime-soda ash neutrolosis study.

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SECTION 8

COUPLED CATION EXCHANGE/REVERSE OSMOSIS AMD TREATMENT SYSTEMS

Due to an inability to use RO as a single unit process to treat Crown AMD (or mine drainages of similar quality) at recoveries greater than 50 percent, the failure of lime neutrolosis as a feasible AMD treatment alternative, and the apparent high cost of soda ash and lime-soda ash neutrolosis processes, it was decided to investigate an AMD treatment scheme which offered a potential for high recovery performance. One promising process appeared to be a coupled CIX/RO system in which an ion exchanger operating on a sodium cycle removes calcium and other +2 valence and +3 valence cations from the AMD, replaces them with sodium ions yielding essentially an Na_2SO_4 - H_2SO_4 solution, and transfers this calcium-free effluent to an RO unit where it can be processed at high recovery.

Such a coupled system was investigated in some detail for treatment of Crown AMD. In addition to the IX background information presented in Section 4, the fundamental principles of the process are noted, and experimental procedures and results of the study are discussed at length in order to provide information to evaluate the merits of the system.

THE CATION EXCHANGE PROCESS

The CIX process is defined as a reversible replacement of the exchangeable cations between a resin and the feed solution, where the exchange resin contains ionic groups which are chemically linked to the polymer structure of the resin in which the reactions occur. The polymeric portion of the resin must be highly cross-linked so that the solubility of the resin is negligible. Moreover, the resin structure must be chemically stable so that essentially no degradation occurs during use.

In particular, the chemical reactions for the sodium-form CIX process, which involves passing an AMD water through a strong-acid exchange resin bed, can be represented as for +2 valence cations follows:

Exhaustion cycle: $MSO_4 + 2R^{C}Na \rightarrow Na_2SO_4 + R^{C}{}_{2}M$

Regeneration cycle: $R^{C}{}_{2}M + 2Na^{+} \rightarrow M^{+2} + 2NaR^{C}$

where M = +2 valence cations in AMD

R^{C} = cation resin matrix.

Principles of Operation

A complete CIX operations cycle contains the following four steps:

Exhaustion Process--

During exhaustion, the AMD to be treated is continuously fed through the bed of IX resin, and the softening capability of the ion exchanger is gradually depleted. The feed flows in the ion exchanger may occur in an upflow or downflow direction. The exhaustion step is normally terminated when the concentrations of the contaminating ions in the effluent reach an undesirable breakthrough level. This level is usually established beforehand and is based on the maximum concentration of undesirable cations allowed in the effluent.

Backwash Process--

Effective backwash is required to maintain a clean resin bed. Regardless of the flow direction of the exhaustion process, the backwash process is accomplished via a strong upward flow of raw water through the IX bed before the regeneration process is applied to restore the capacity of the bed for subsequent treatment.

The purpose of the backwash process is to expand the IX bed and to break up any channels that may have formed in the column. In order to avoid loss of resin in backwash, attention must be given to the expansion characteristics of the bed. In addition, backwash is applied to separate the particles and release any insoluble matter which may have collected in the bed during the softening run.

Regeneration Process--

The regeneration process is applied to restore the capacity of the ion exchanger by passing a regenerant solution through the exhausted resin bed. The flow of the regenerant solution may be upflow or downflow. By definition, counter-current operation has exhaustion in one direction and regeneration in the opposite direction, while co-current operation has exhaustion and regeneration in the same direction. Further, it has been recognized that counter-current flow may result in more efficient operation (28), since lower ion leakages and higher regenerant utilizations can be obtained.

For optimum regeneration, the regenerant must have adequate residence time to diffuse into the interior of the bed and then displace the ionic groups of the resin. If the regeneration flow rate is too rapid, this process may not be complete due to insufficient contact time; if too slow, the service time will be too long, and a greater resin inventory will be required. Therefore, it is important to determine the proper regenerant flow rate. The time needed for the regeneration process depends on the flow rate, resin volume, resin type, regenerant concentration, and salt dosage.

Rinse Process--

After the regenerant solution has been applied to the ion exchanger, the water or liquid to be treated is used to rinse the IX bed before it is returned to the exhaustion process. The purpose of the rinse process is to complete the contacting and remove spent regenerant from the ion exchanger. Normally, the rinse direction is the same as that of the regeneration. A complete rinse operation is accomplished by two procedures: a slow rinse followed by a fast rinse. Since the regenerant must be removed gradually through the ion exchanger to assure proper contact time required for an efficient and economical regeneration, the slow rinse is usually operated at approximately that rate used in regeneration. Subsequently, the rinse rate is increased to quickly remove the last traces of regenerant, thus completing the cycle.

Leakage and Capacity

During exhaustion, the unwanted ions are progressively removed as the feed flows through the exchange resin bed. The purity of the softened effluent is determined by the concentration difference between the cations in the water and the ions on the resin at the bottom of the IX bed (for downflow operation). From a materials-cost viewpoint, the amount of regenerant required for a complete regeneration (which means complete freedom from the unwanted ions in the lowest portion of the exchange bed) of an exhausted exchange resin bed is uneconomical; therefore, some escape of undesirable ions into the effluent is to be expected. This escape is known as ion leakage. The major variable affecting the ion leakage is the quantity of the regenerant applied during the regeneration. Lower leakage rates can be obtained as more regenerant is used.

The capacity (C) of the IX resin bed can be calculated from the volume Q in liters (l) of AMD water treated, the volume (V) of the IX resin in cubic meters (m^3), and the concentration L in mg/l as $CaCO_3$ of contaminants being removed during the exhaustion process. The variable L can be approximated by computing the "loading factor" of AMD treated (within some range of experimental error). The formula for the capacity is

$$C = \frac{Q \times L}{V \times 10^6},$$

where C is expressed in units of kg as $CaCO_3/m^3$.

There are many factors which influence IX capacity, as well as ion leakage, such as salt dosage, regenerant concentration, AMD composition, exhaustion flow rate, etc. (29). But like ion leakage, the most important factor in evaluating capacity is the amount of regenerant (salt dosage) used. The IX capacity increases asymptotically to a maximum as the salt dosage is increased, while the regenerant utilization (a measure of the efficiency of a dosage of salt to restore bed capacity) decreases with increasing salt dosage. It is found that the optimum concentration range of salt in regenerant solution which will produce the maximum exchange capacity lies between 10 and 15 percent by weight; and increases in exhaustion flow rate up to 22.3 lps/m^3 (10 gpm/ft^3) will have little effect on the capacities obtained since the ion exchange occurs so rapidly in the resin (22).

THE COUPLED CATION EXCHANGE/REVERSE OSMOSIS PROCESS

Although the RO process has been found to be feasible for treating AMD, high-recovery operation is usually limited by calcium sulfate and/or iron fouling problems. In order to maximize the recovery rate of an RO process and to potentially ease the difficult waste effluent disposal problem, a coupled IX/RO system can be used to treat AMD waters. In this system the ion exchanger acts as a pretreatment step for the RO process. AMD raw feed is initially pretreated by a sodium-form IX resin bed in which a large fraction of the cationic pollutants are removed and replaced by sodium ions. Then this softened effluent is fed into the RO unit, where the possibility of membrane fouling is greatly decreased and high recoveries can be obtained.

Because of the high product water recovery that can now be obtained from the coupled IX/RO process, the volume of the waste brine obtained is also decreased. Moreover, the concentration of Na_2SO_4 in this waste brine is high enough to assist with the regeneration of the exhausted IX resin. In this mode, the brine is stored and later recycled back to the IX unit to make up a portion of the regenerant stream.

EXPERIMENTAL PROCEDURES AND RESULTS

Ion Exchange System

Experiments were initially conducted with the IX unit alone in order to investigate the characteristics of the sodium-form, strong-acid cation exchanger. Information was obtained concerning the free mineral acidity (FMA) of the IX effluent, the leakage of hardness-forming ions from the exchanger, the treatment capacity of the IX resin, and the utilization efficiency of the regenerant solutions. TABLE 14 presents basic CIX operating parameters used during the study.

TABLE 14. OPERATING CONDITIONS OF THE ION EXCHANGE SYSTEM*

Volume of Resin	0.41 m^3 (14.5 ft^3)
Service Cycle Flow Direction	Downflow
Service Cycle Flowrate	0.22-0.25 liter/sec (3.5-3.9 gpm)
Backwash Flow Direction	Upflow
Backwash Cycle Flowrate	1.0-1.1 liter/sec (16-18 gpm)
Regenerant Flow Direction	Downflow
Regenerant Flowrate	0.27 liter/sec (4.3 gpm)
Slow Rinse Flow Direction	Downflow
Slow Rinse Flowrate	0.13 liter/sec (2.0 gpm)
Fast Rinse Flow Direction	Downflow
Fast Rinse Flowrate	1.3 liter/sec (20 gpm)

*15-percent NaCl solution regeneration.

Initial experimental results were erratic because of the time varying AMD loading factor, which created a problem in calculating the actual resin capacity. To correct for this, an AMD composite was collected for each exhaustion run using an automatic sampler which drew specimens of raw AMD at preset time intervals during the run. The composite loading factor was then used to represent the average AMD water quality treated during the exhaustion process. Figure 34 illustrates the loading factor variation of exchangeable AMD cations encountered during the course of the experiments. The average constituent concentrations during the 100-day period of experimental studies are presented in TABLE 15, where the averaged loading factor of the exchangeable valence +2 and +3 cations shown in TABLE 15 is approximately 1950 mg/l as $CaCO_3$.

TABLE 15. AVERAGE COMPOSITION OF CROWN AMD DURING 100 DAY PERIOD 5/25/75 TO 9/2/75

Component	Concentration (mg/l)
Ca	380
Mg	110
Al	4.4
Ferrous Fe	250
Mn	4.5
Na	480
Total Fe	270
SO_4	2900
pH	4.5

The results which follow were obtained when only NaCl solution was utilized in the regeneration cycle. These form the data base for the subsequent evaluation of the coupled system.

FMA and Leakage Results at Various NaCl Dosages--

Figure 35 contains the FMA data obtained at salt (NaCl) dosages of 128, 160, and 240 kg/m^3 (8, 10, and 15 lb/ft^3). The observations indicate that the FMA of the AMD was removed almost completely during the first 20 percent of the run. Then, hydrogen absorbed at the beginning of the exhaustion process began to be displaced by the incoming ions through the next 30 percent of the run, and was finally stabilized during the last 50 percent of the exhaustion cycle. This characteristic of the sodium-form strong-acid IX resin was further identified by the variation of pH value of the softened feed throughout the exhaustion process. These FMA results are in agreement with studies made by the Culligan International Company on a sodium-form cation exchanger (15). It was also noted that the FMA curves are all similar in shape and independent of the regenerant dosages used, indicating that the phenomena of hydrogen removal was qualitatively the same for the salt dosages utilized in this research.

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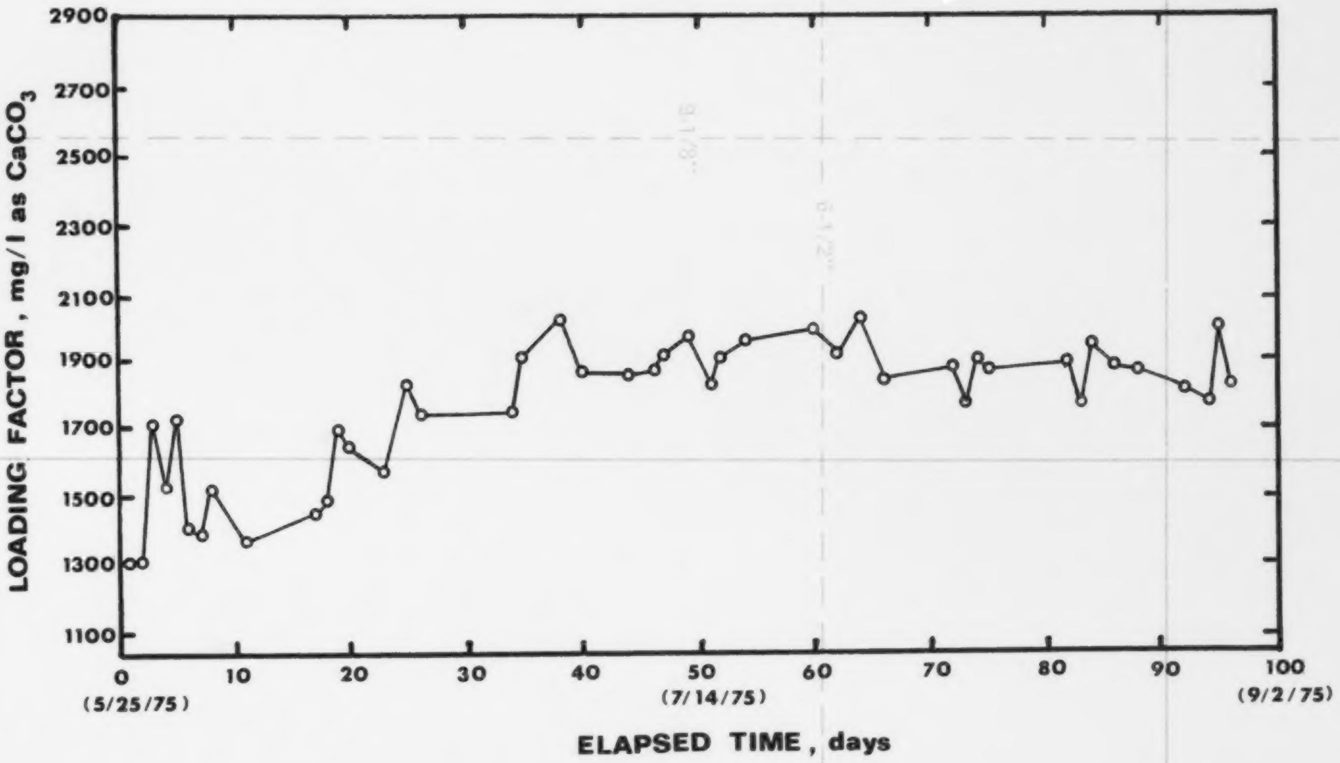

Figure 34. AMD loading factor versus time.

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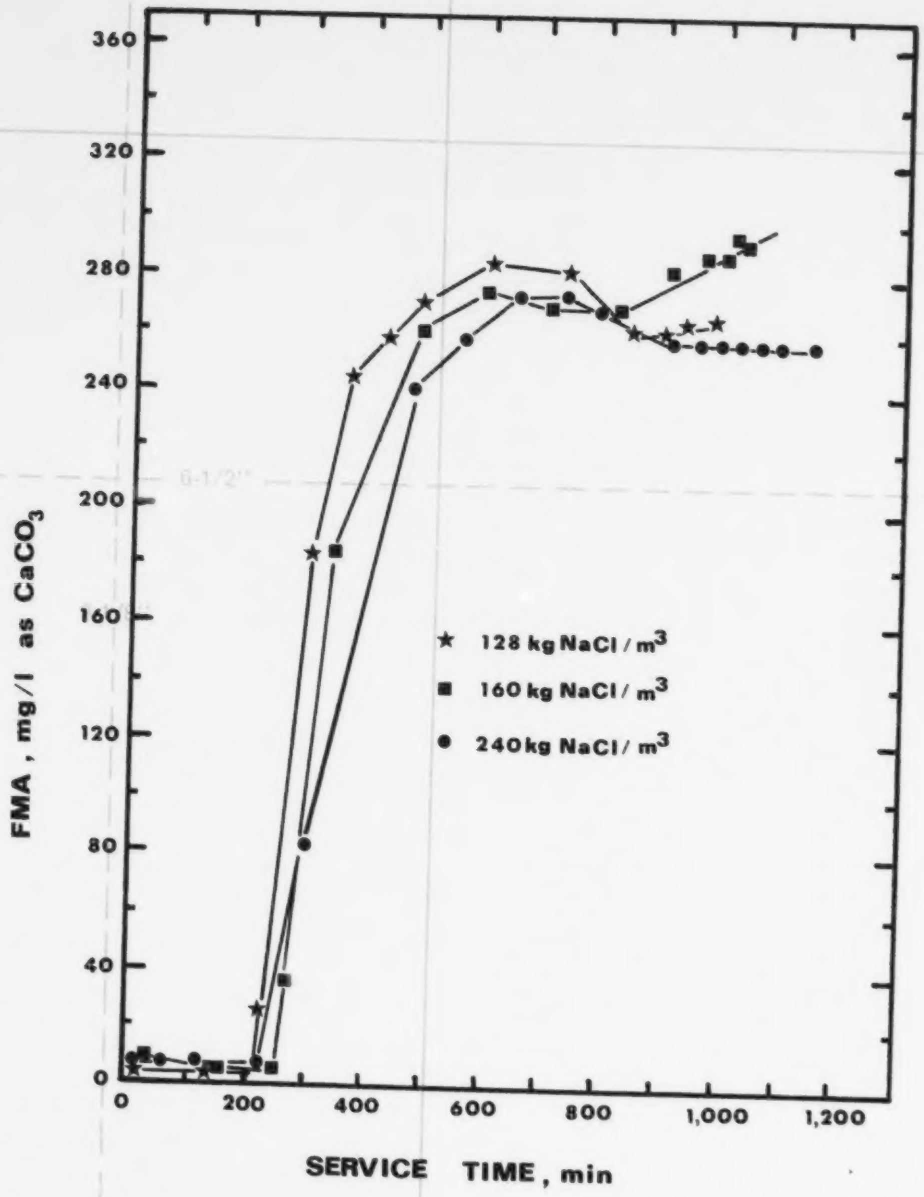

Figure 35. FMA versus time in the CIX effluent.

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Leakage Data at Various NaCl Dosages--

It is known that one of the most important variables influencing the leakage is the amount of salt dosage used during regeneration. Figures 36, 37, and 38 illustrate the comparable calcium, magnesium, and total hardness leakage versus time curves during the exhaustion process at three different salt dosages. The concentrations of calcium and magnesium in the softened water at an NaCl dosage of 240 kg/m^3 (15 lb/ft^3) were found to be much lower than those obtained at dosages of 160 and 128 kg/m^3 (10 and 8 lb/ft^3). This verifed that lower ion leakages were obtained at higher salt dosages due to the higher conversion of the exchange resin to the sodium form.

It was also interesting to observe that during the exhaustion process the leakage was high at the onset of the run, then dropped to a minimum, and rose again in the vicinity of the exhaustion breakthrough point. This characteristic of the leakage curve can be explained qualitatively. At the very beginning of the service cycle the effluent from the IX system was in fact a portion of the water fed into the exchanger at the end of the fast rinse process. Since AMD was used in the fast rinse cycle, not enough contact time existed between this AMD water and the exchange resins, resulting in high leakage observed at the beginning of the exhaustion process. Follow-this effect, the leakage dropped due to the increase in contact time between the AMD and the resin. This drop was initially abrupt and subsequently showed a gradual decrease over a major portion of the exhaustion cycle. During this period, the cations in the AMD influent were exchanged for the sodium ions at the top of the bed, and the released sodium ions then exchanged with the cations in the bottom of the bed due to the incomplete co-current regeneration. As the run progressed, this leakage continued to decrease as the cations in the bottom of the bed were gradually consumed until the exhaustion front neared the end of the resin and the resulting insufficient contact time caused increased leakage. The magnitude (slope) of this decrease was found to be a function of salt dosage. As expected at the breakthrough point, the IX column was exhausted and the leakage rose sharply.

Capacities and Regenerant Utilizations at Various NaCl Dosages--

The solid line in Figure 39 represents the relationship between the capacity and the NaCl dosage with the corresponding regenerant utilization curve shown as a solid line in Figure 40. The results show that the IX capacity increased as the salt dosage increased, while the regenerant utilization decreased with increasing salt dosage. For example, capacities of 71.0 and 59.5 kg $CaCO_3$/m^3 (31.0 and 26.0 kgr $CaCO_3$/ft^3) were obtained from Figure 39 at NaCl dosages of 240 and 128 kg/m^3 (15 and 8 lb/ft^3), respectively, while Figure 40 showed the average regenerant utilization of 34.4 percent at 240 kg/m^3 (15 lb/ft^3) was much lower than that of 54.2 percent at 128 kg/m^3 (8 lb/ft^3). The individual data points shown in Figures 39 and 40 were calculated from experimental information of the type presented in TABLE 16 for two selected runs.

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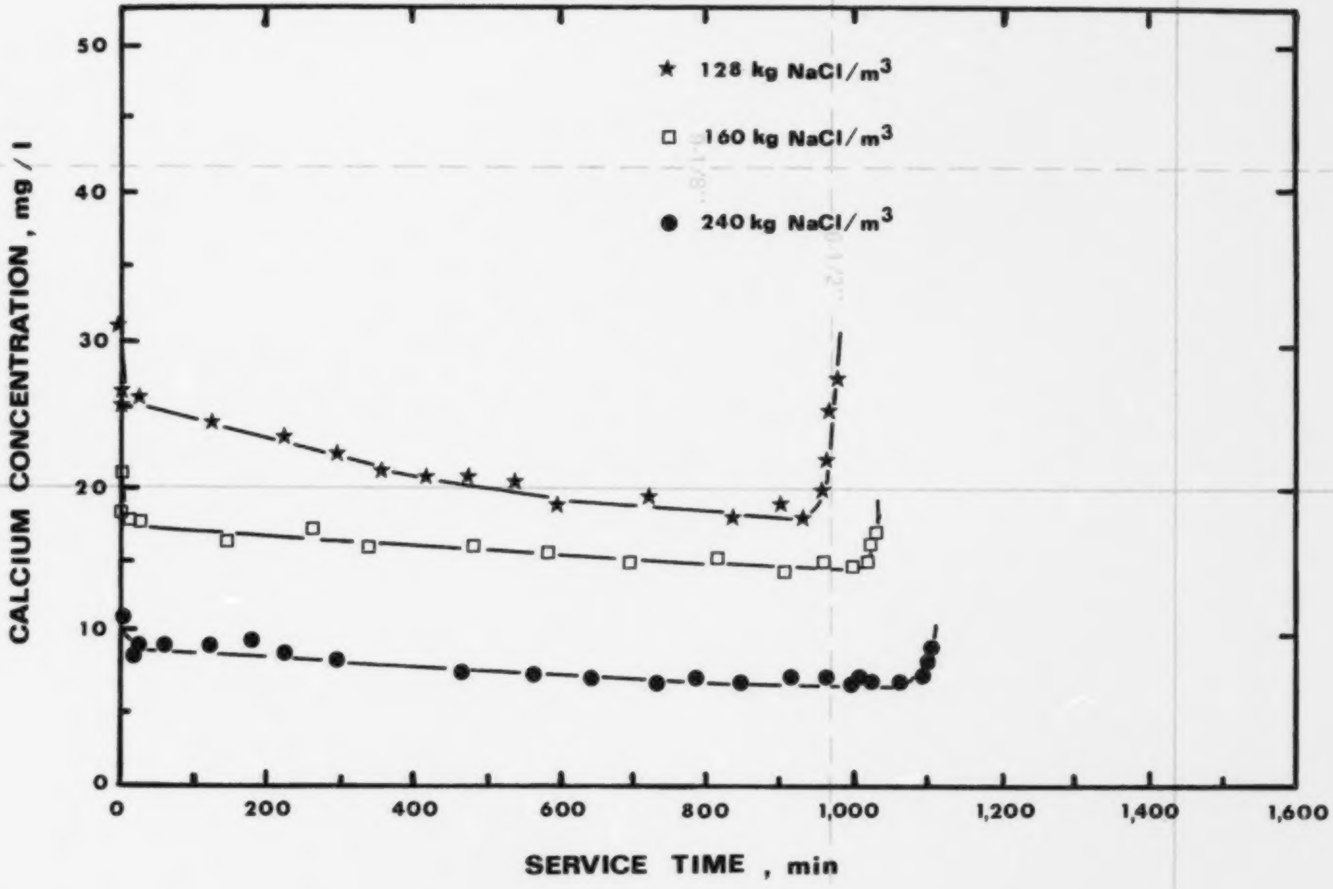

Figure 36. Calcium leakage profile.

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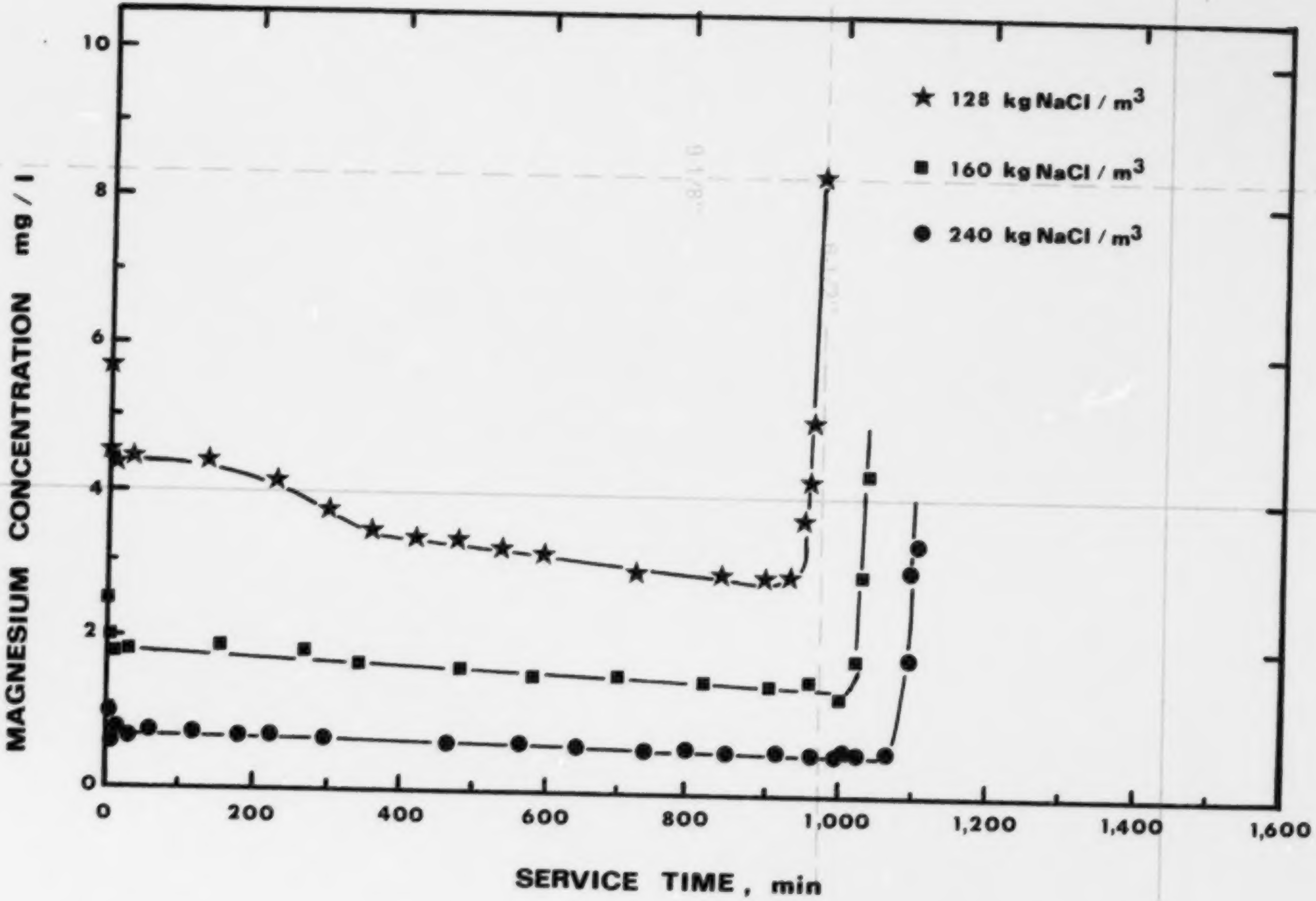

Figure 37. Magnesium leakage profile.

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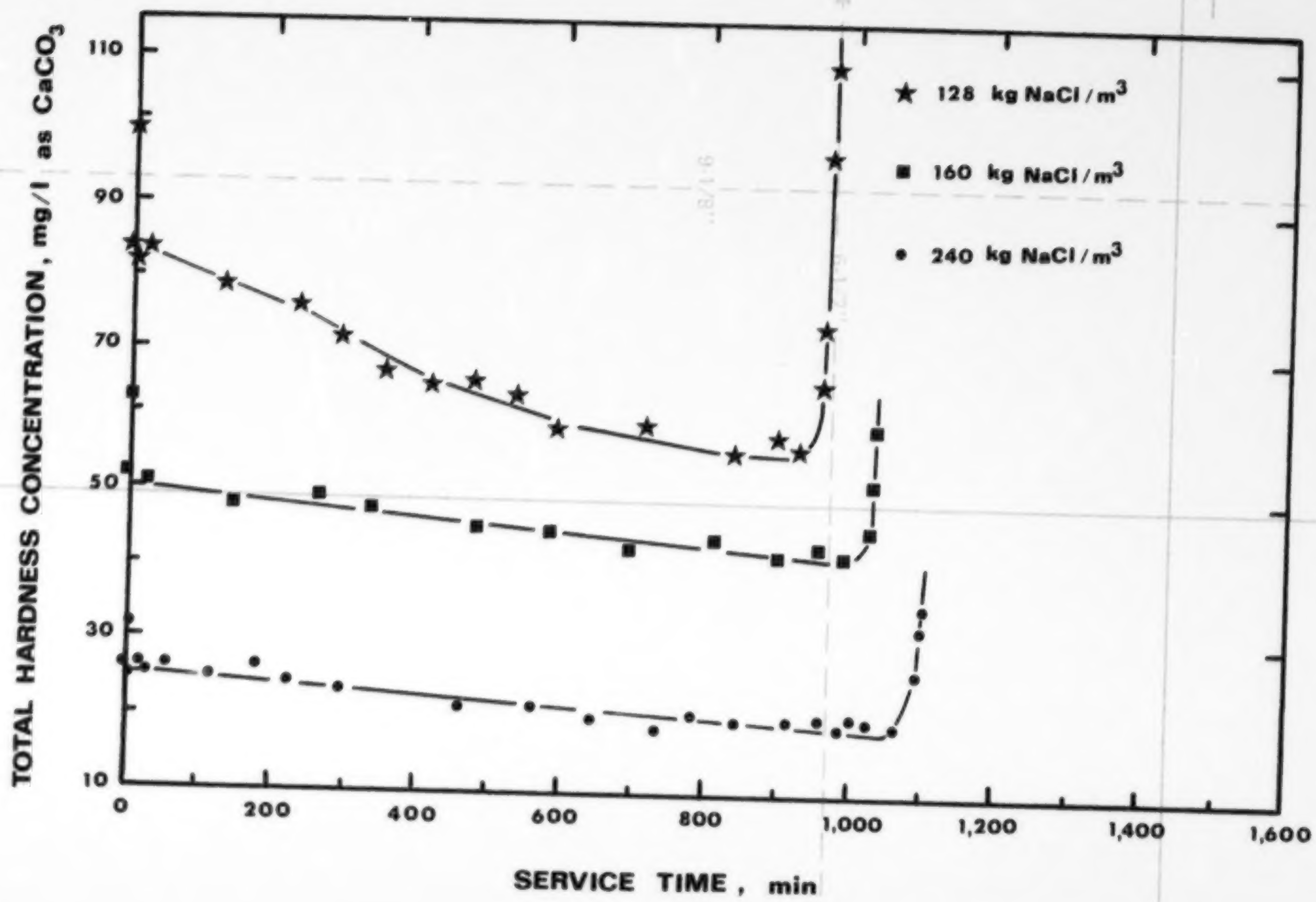

Figure 38. Total hardness leakage profile.

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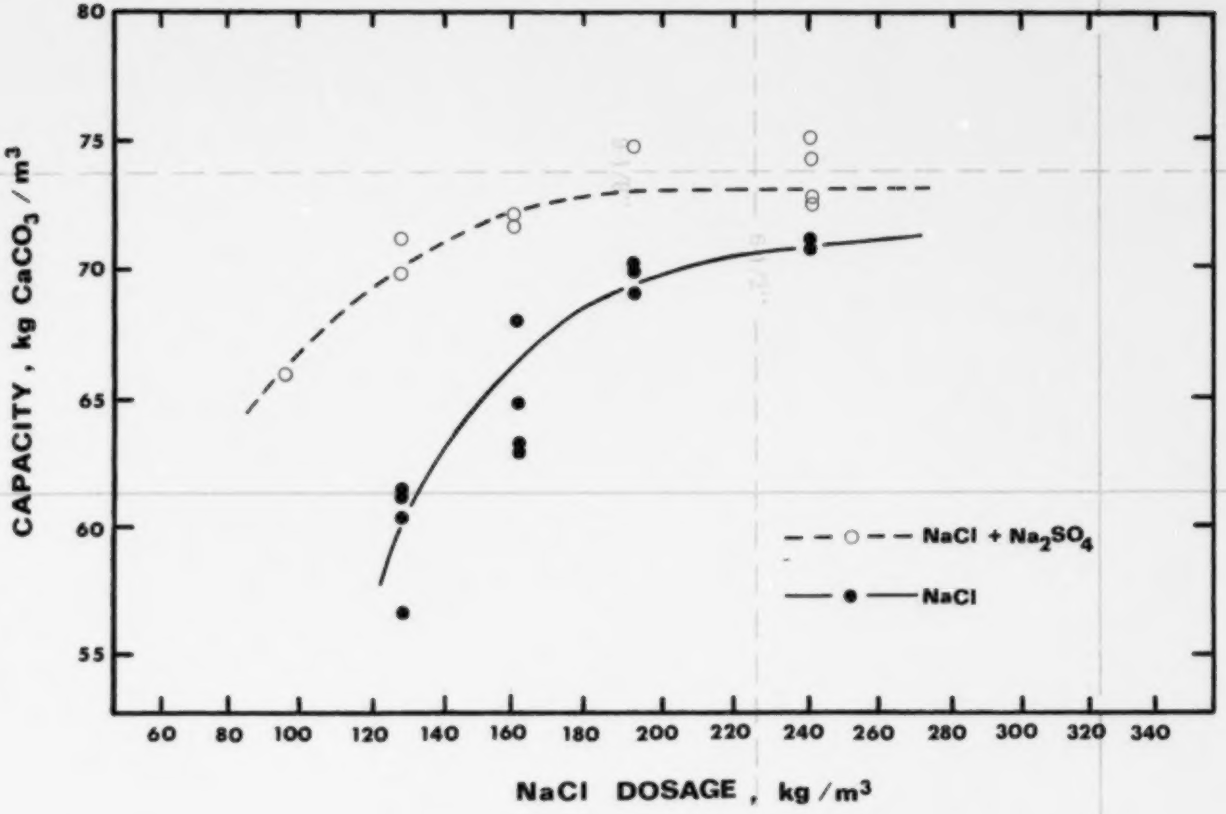

Figure 39. Effect of salt dosage on resin capacity.

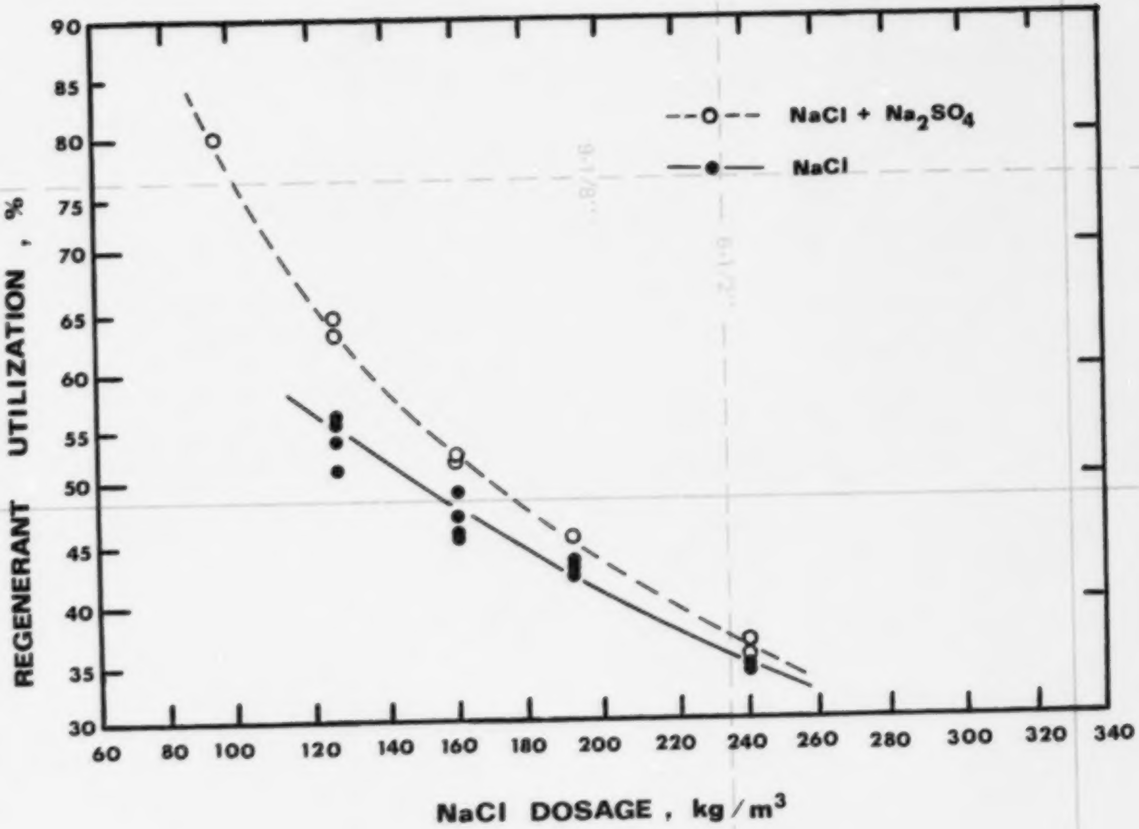

Figure 40. Effect of salt dosage on regenerant utilization.

TABLE 16. CAPACITY AND REGENERANT UTILIZATION DATA

Run No.	Na^+ in RO Brine, mg/l*	Volume of RO Brine, liters (gallons)*	NaCl Dosage, kg/m^3 (lb/ft^3)*	Service Cycle Flow Rate, lpm (gpm)	Service Cycle Run Time, min	Loading Factor mg$CaCO_3$/l (gpg)
2	–	–	240 (15)	4.35 (3.79)	1,301	1,568 (91.5)
7	16,600	1,143 (302)	96 (6)	14.57 (3.85)	999	1,859 (108.5)

*Used in the regeneration process prior to cited Run No.

Data from Run No. 2 is used to illustrate a capacity and regenerant utilization calculation.

For $Q = (14.35 \text{ lpm}) \times (1301 \text{ min}) = 18{,}670 \text{ l}$,
$V = 0.41 \text{ m}^3$ (the volume of the resin bed),
$L = 1{,}568 \text{ mg/l}$,

and with Q, V, and L, expressed in the above units, and the capacity (C) in kg $CaCO_3/m^3$ given by

$$C = \frac{Q \times L}{V \times 10^6},$$

then,

$$C = \frac{(18{,}760) \times (1{,}568)}{(0.41) \times 10^6} = \boxed{71.7 \text{ kg } CaCO_3/m^3}.$$

The amount of regenerant used prior to Run No. 2 is

$$(240 \text{ kg } NaCl/m^3) \times (23 \text{ kg } Na/58.5 \text{ kg } NaCl)$$

$$= 94.4 \text{ kg } Na/m^3.$$

This must be converted to a $CaCO_3$ equivalent value. The factor for sodium is 2.17, and the Na usage is

$$(94.4 \text{ kg } Na/m^3) \times \left(2.17 \frac{\text{kg } CaCO_3}{\text{kg } Na}\right) = 204.8 \text{ kg } CaCO_3/m^3.$$

The regenerant utilization is then,

$$\frac{71.7 \text{ kg } CaCO_3/m^3}{204.8 \text{ kg } CaCO_3/m^3} \times 100\% = \boxed{35.0\%}.$$

For larger salt dosage the conversion of the exhausted bed did yield a higher capacity, but the increase was obtained at a sacrifice in the efficiency of salt usage. This fact is illustrated in the calculated regenerant utilization which shows that the increase in the measured capacity is not as fast as that of the theoretical capacity; thus, more regenerant is wasted at higher dosages. It should be noted that the regenerant utilization percentages presented throughout these studies were calculated on the theoretical capacity for NaCl alone.

CIX/RO System

In this series of studies, the CIX system was coupled to the RO unit to provide combined treatment of the AMD water. The softened effluent from the ion exchanger was fed to the RO unit and produced nearly potable water at recoveries exceeding 90 percent. The concentrated Na_2SO_4 waste brine from the RO unit was fed to a waste brine storage tank and used as a "regenerant aid" during the regeneration process. Figure 41 displays a flowsheet for this system for an exhaustion process operating at 91.3-percent recovery [(Product/AMD Feed) x 100 %].

Samples of softened feed, blended feed, brine, composite brine, and product were also taken and analyzed during the experiments. In addition, samples of softened water from the IX unit were collected at intervals throughout the exhaustion process. Two salt dosages of 128 and 240 kg/m^3 (8 and 15 lb/ft^3) NaCl solution plus Na_2SO_4 waste brine were used to obtain leakage data; and NaCl dosages at 90, 128, 160, 190, and 240 kg/m^3 (6, 8, 10, 12, and 15 lb/ft^3) plus Na_2SO_4 waste brine were utilized to evaluate IX capacity and regenerant utilization phenomena.

Overall System Performance--

Observations made during the course of the experimental work indicated that high permeate recoveries (90 to 93 percent) could be maintained in the RO unit throughout the period of operation without any evidence of membrane fouling. The performance of the coupled system can be analyzed using TABLE 17, which presents a representative chemical analysis of AMD feed, softened feed, blended feed, brine, and product at a salt dosage of 240 kg/m^3 (15 lbs $NaCl/ft^3$). TABLE 17 also presents the salt rejections for each specific ion.

Using equation (B35) presented in Appendix B, a saturation factor value of 0.55 was determined for the calcium sulfate present in the brine of TABLE 17. Since a factor less than 1.0 indicates that no precipitation should occur, the absence of precipitation in the RO unit was in agreement with expected behavior.

It was also found that the salt rejections of all constituents based on the blended feed were over 99 percent, while those based on the softened feed have lower values. It should be noted that the rejections in the blended and softened feeds might be closer in value in an RO unit requiring a lower recycle rate. In the 4K unit it is necessary to recycle a considerable amount of the brine in order to attain a high recovery level. This means that although the membranes reject over 99 percent of the ions to which they are exposed, the overall rejection is lower because the membrane "sees" a higher average ion concentration than would be the case if no brine recycle were necessary.

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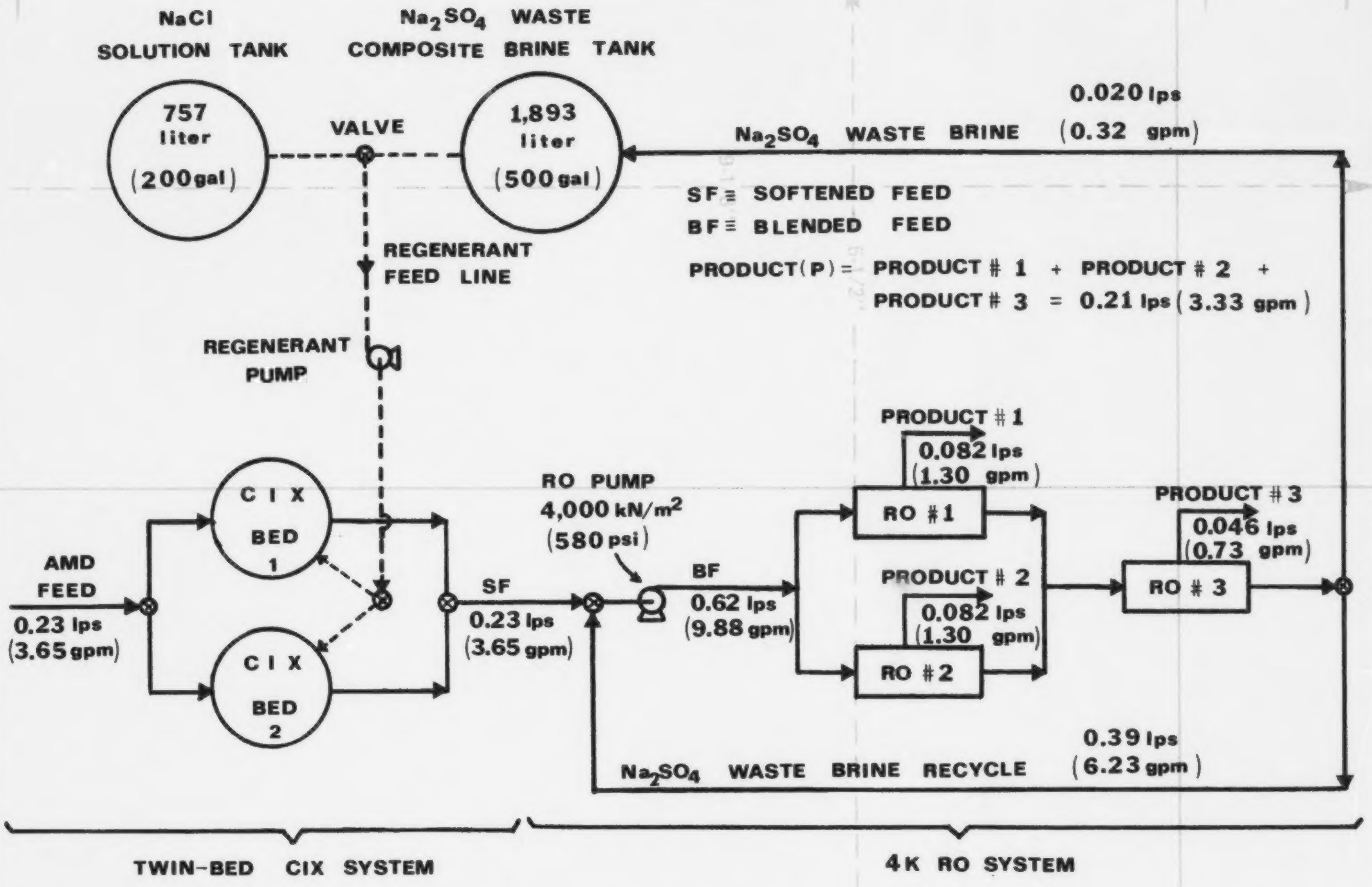
NaCl SOLUTION TANK
757 liter (200 gal)
VALVE
Na_2SO_4 WASTE COMPOSITE BRINE TANK
1,893 liter (500 gal)
Na_2SO_4 WASTE BRINE
0.020 lps (0.32 gpm)
SF ≡ SOFTENED FEED
BF ≡ BLENDED FEED
PRODUCT(P) = PRODUCT # 1 + PRODUCT # 2 + PRODUCT # 3 = 0.21 lps (3.33 gpm)
REGENERANT FEED LINE
REGENERANT PUMP
AMD FEED
0.23 lps (3.65 gpm)
C I X BED 1
C I X BED 2
SF
0.23 lps (3.65 gpm)
RO PUMP
4,000 kN/m^2 (580 psi)
BF
0.62 lps (9.88 gpm)
PRODUCT # 1
0.082 lps (1.30 gpm)
RO #1
PRODUCT # 2
0.082 lps (1.30 gpm)
RO #2
PRODUCT # 3
0.046 lps (0.73 gpm)
RO # 3
Na_2SO_4 WASTE BRINE RECYCLE
0.39 lps (6.23 gpm)
TWIN-BED CIX SYSTEM
4K RO SYSTEM

Figure 41. Flowsheet of the coupled IX-RO system at 26.7 °C (80 °F) operating at 91.3% recovery (P/SF).

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TABLE 17. REPRESENTATIVE CHEMISTRY ANALYSIS AT A SALT DOSAGE OF 240 kg/m^3 (15 lb/ft^3)

Component	AMD Water	Softened Feed (SF)	Blended Feed (BF)	Brine	Product	Salt Rejection* in SF (%)	Salt Rejection* in BF (%)	Salt Rejection* in AMD (%)
Ca	380	6.0	45	71	0.2	96.7	99.6	>99.9
Mg	110	0.6	4.6	7.0	0.01	98.3	99.8	>99.9
Al	4.4	0.2	0.9	1.2	trace	>99.9	>99.9	>99.9
Ferrous Fe	250	2.5	12	18	trace	>99.9	>99.9	>99.9
Mn	4.5	0.02	0.2	0.4	trace	>99.9	>99.9	>99.9
Na	480	1,200	8,200	12,000	58	95.2	99.3	87.9
Total Fe	270	2.6	12	19	0.01	99.6	99.9	>99.9
SO_4	2,900	2,900	28,000	48,000	260	91.0	99.1	91.0
Conductance	3,800	5,500	27,000	40,000	650	88.2	97.6	82.9
pH	4.5	2.8	2.7	2.5	3.4			

All units are mg/l except pH and conductance (Mmhos/cm).

$$^{*}\text{Salt Rejection (\%)} = \frac{\text{Feed (SF, BF, AMD) - Product}}{\text{Feed (SF, BF, AMD)}} \times 100\%$$

In addition, the product water quality produced from the coupled IX/RO system was quite good except for the sodium and sulfate contents. (Note that all other AMD constituent rejections were greater than 99.9 percent.) These high concentrations of sodium and sulfate in the product were due, of course, to the existence of extremely high concentrations of sodium sulfate in the RO brine side while operating at recoveries over 90 percent.

Effect of Na_2SO_4 Waste Brine on Hardness Leakage--

During the investigation of the coupled system, efforts were made to determine the effects of concentrated Na_2SO_4 waste brine on the regeneration of the IX resin. This was accomplished by continually decreasing the amount of NaCl used in the regeneration step and following this with the injection of all the Na_2SO_4 waste brine produced during the previous exhaustion cycle. The measured effects of this procedure were then determined on the subsequent cycle. (Note the footnote to TABLE 16).

Figure 42 illustrates the total hardness leakage versus time curves at salt dosages of 128 kg NaCl/m^3 (8 lb/ft^3), 128 kg NaCl/m^3 plus Na_2SO_4, 240 kg NaCl/m^3 (15 lb NaCl/ft^3), and 240 kg NaCl/m^3 plus Na_2SO_4. It was found that the use of Na_2SO_4 waste brine as a regenerant aid decreased the hardness leakage of the discharged effluent, and that the relative magnitude of the effect of the Na_2SO_4 regenerant aid on the hardness leakage at an NaCl dosage at 128 kg/m^3 (8 lb/ft^3) was apparently higher than that at 240 kg/m^3 (15 lb/ft^3). This tendency can be noted more readily from Figure 43 which presents the calcium, magnesium, and total hardness leakage obtained at different dosages. This can be explained by the fact that an asymptotic hardness leakage seems to be approached around salt dosages of 240 kg NaCl/m^3 (15 lb NaCl/ft^3) plus 51 kg Na/m^3 (3.2 lb Na/ft^3), which represents Na levels in the average amount of Na_2SO_4 waste brine used.* Much higher leakages are observed at 128 kg/m^3 (8 lb/ft^3) pure NaCl salt dosages when compared to this asymptotic value; therefore, it appears that the use of the Na_2SO_4 regenerant aid can effectively decrease this leakage. Moreover, since the leakage obtained at 240 kg NaCl/m^3 (15 lb NaCl/ft^3) is already approaching this asymptotic value, the addition of the regenerant aid does not have much effect on leakage decrease. Quantitative comparisons using Figure 43 illustrate that the hardness leakage drop from 128 kg NaCl/m^3 to 128 kg NaCl/m^3 plus Na_2SO_4 is about ten times that from 240 kg NaCl/m^3 to 240 kg NaCl/m^3 plus Na_2SO_4. The phenomenon of the asymptotic leakage being approached for a salt dosage of 240 kg NaCl/m^3 (15 lb NaCl/ft^3) plus Na_2SO_4 also implies that in a practical co-current operation, complete regeneration of an exhausted ion exchanger is difficult to accomplish.

Effect of Na_2SO_4 Waste Brine on Capacity and Regenerant Utilization--

Starting with the baseline capacity curve obtained using only NaCl as the regenerant, a comparable curve was established to measure the effect of

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*Amounts of Na in the Na_2SO_4 waste brine utilized in regenerant aid runs ranged from 46 to 54 kg/m^3 (2.9 to 3.4 lb/ft^3) per run.

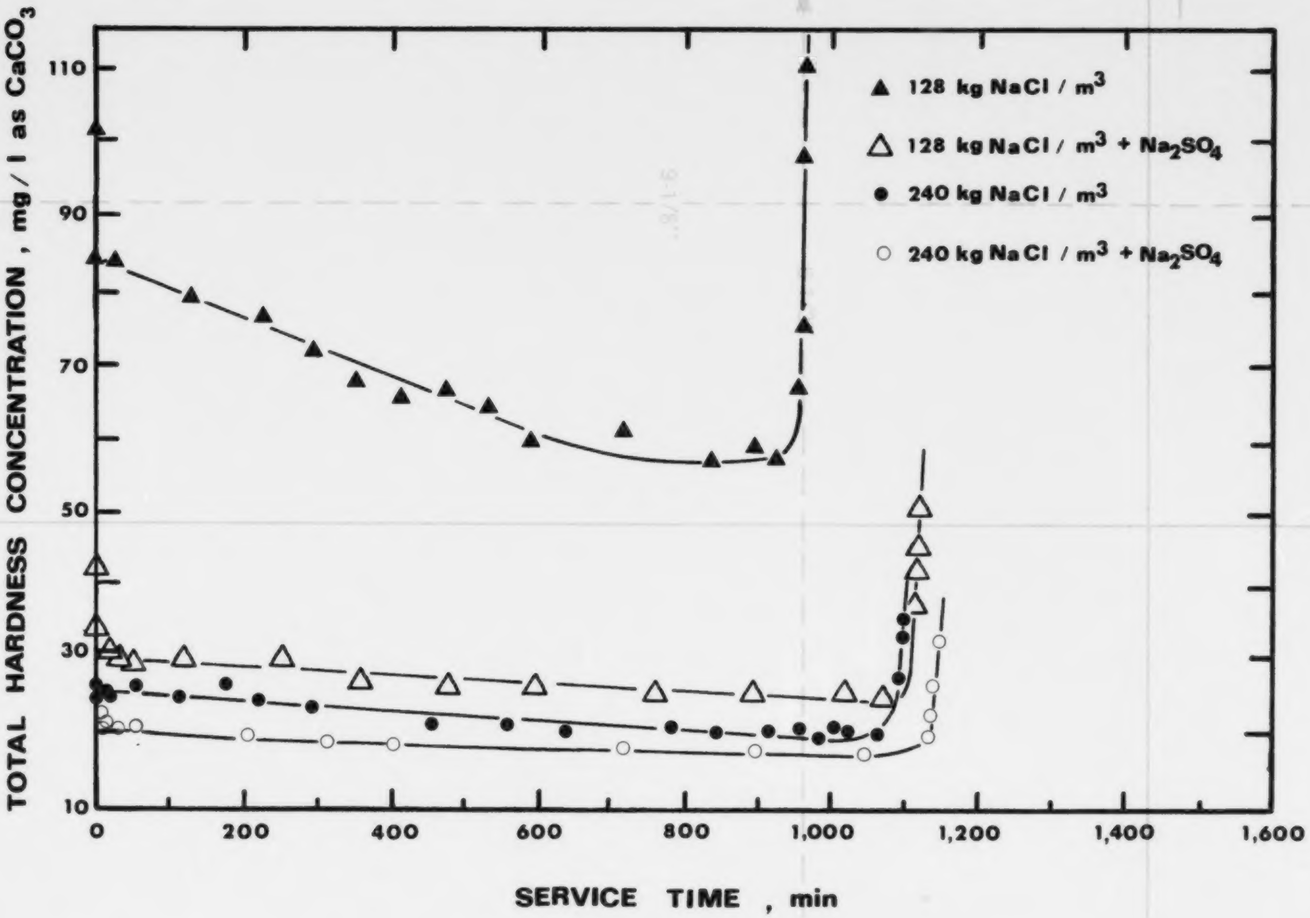

Figure 42. Effect of Na_2SO_4 waste brine on the total hardness leakage profile.

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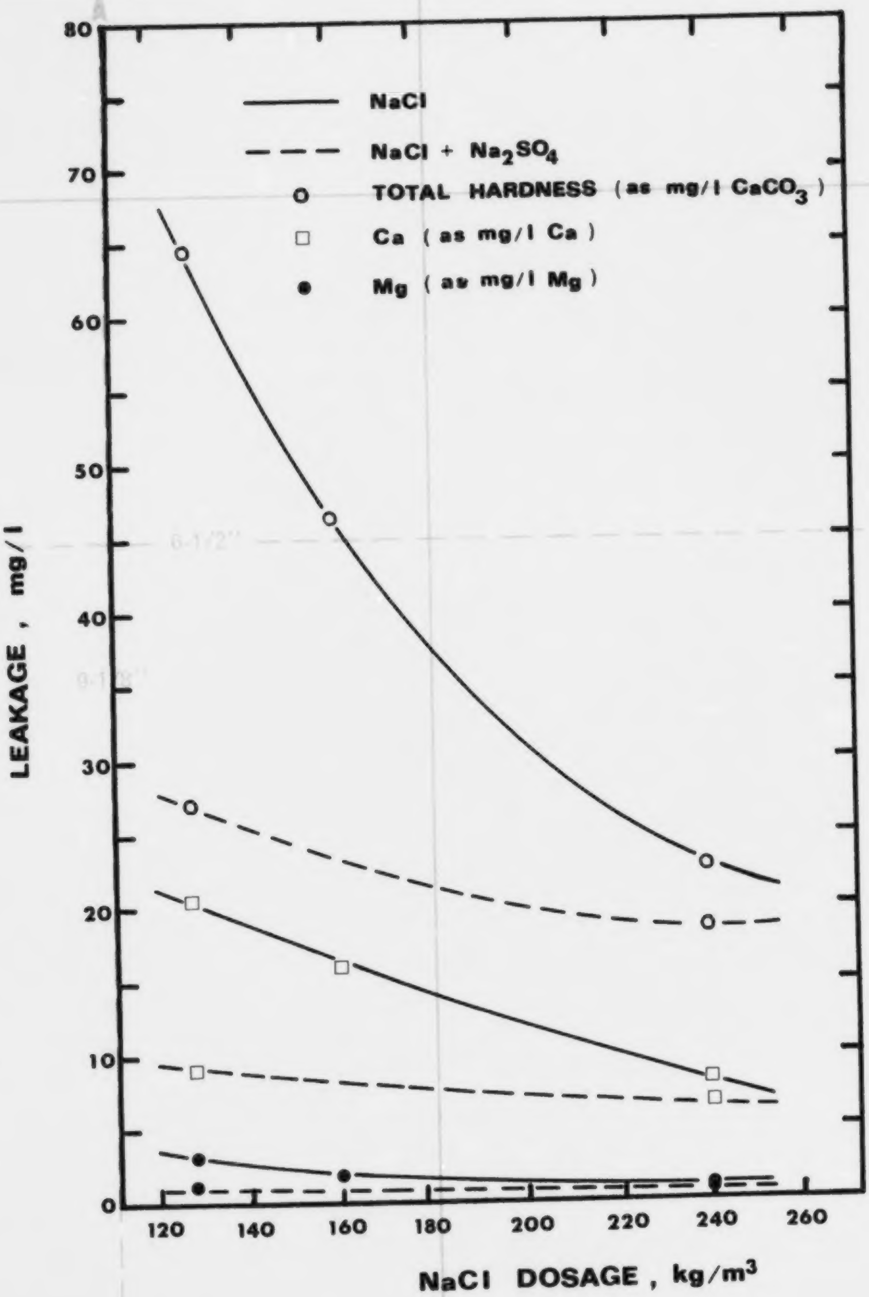

Figure 43. Effect of salt dosage on calcium, magnesium, and total hardness leakages.

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Na_2SO_4 on the capacity. The dashed line in Figure 39 represents those capacities obtained at dosages of 96, 128, 160, 192, and 240 kg $NaCl/m^3$ (6, 8, 10, 12 and 15 lb $NaCl/ft^3$) plus Na_2SO_4. The corresponding regenerant utilization curve is illustrated as a dashed line in Figure 40. Data points for the dashed curves are generated using information of the type provided for Run No. 7 in TABLE 16. In this case, calculations for Run No. 7 would yield C = 66.0 kg $CaCO_3/m^3$ with a regenerant utilization of 80.6 percent.

An investigation of the capacity and regenerant utilization curves indicates that higher capacities and higher regenerant utilizations were obtained with the use of Na_2SO_4 waste brine. It was found that the capacity approached an asymptotic value of 73.3 kg $CaCO_3/m^3$ (32.0 kgr $CaCO_3/ft^3$) at a dosage of 240 kg $NaCl/m^3$ (15 lb $NaCl/ft^3$) plus 51 kg Na/m^3 (3.2 lb Na/ft^3) of Na_2SO_4 waste brine. The use of any salt dosage higher than this limit would seem to have little effect on the capacity. It is also important to note that at a salt dosage of 96 kg $NaCl/m^3$ (6 lb $NaCl/ft^3$) plus Na_2SO_4, a regenerant utilization as high as 80 percent was obtained, with a capacity of 66.0 kg $CaCO_3/m^3$ (28.8 kgr $CaCO_3/ft^3$), i.e. the salt dosage required was only 125 percent of the theoretical quantity. This implies an economical value by using Na_2SO_4 waste brine as a regenerant aid since the quantity of salt required to regenerate an exhausted sodium form ion exchanger is usually 250-350 percent of the theoretical quantity.

Overall it was noted that an NaCl dosage savings of approximately 40 percent could be obtained with the aid of Na_2SO_4 waste brine. This was done by investigating comparable capacities with and without the regenerant aid. For example, a capacity of 66.4 kg $CaCO_3/m^3$ (29 kgr $CaCO_3/ft^3$) could be achieved using either 99 kg $NaCl/m^3$ (6.2 lb $NaCl/ft^3$) plus Na_2SO_4 or 160 kg $NaCl/m^3$ (10 lb $NaCl/ft^3$), the former representing a savings of 61 kilograms $NaCl/m^3$.

TABLE 18 presents the ion exchange capacities and regenerant utilizations obtained from corresponding curves in Figures 39 and 40. It should be noted that the capacity curves obtained are based on the average values at each salt dosage except that 192 kg $NaCl/m^3$ (12 lb $NaCl/ft^3$) plus Na_2SO_4, where only one capacity data point was obtained. Its value appeared unreasonably high in view of the consistently reproducible values obtained at other salt dosages plus Na_2SO_4 combinations. As a result of this correction, it is found that the capacity data obtained in these experiments are within 5 percent of the values shown in TABLE 18. This appears to be a reasonable experimental error in view of the errors potentially introduced by flowrate measurements, hardness monitor changes, etc. Therefore, the curves obtained not only demonstrate the relationship between capacity and salt dosage, but also illustrate that Na_2SO_4 waste brine can be an effective aid in the regeneration of a coupled IX/RO system.

One problem anticipated in the operation of the coupled system was $CaSO_4$ precipitation during the regeneration of the ion exchange bed. Since the Na_2SO_4 waste brine had a sulfate concentration of the order of 35,000 mg/l and higher, precipitation problems were expected with the large amount of calcium ions in the bed at the end of an exhaustion cycle. This was especially true in the case of the co-current type operation utilized in

TABLE 18. COMPARISON OF CAPACITY AND REGENERANT UTILIZATION AT DIFFERENT SALT DOSAGES

Salt Dosage (kg NaCl/m^3)	Capacity (g $CaCO_3$/m^3)	Percent Regenerant Utilization
128	59.5	54.2
160	66.4	48.3
192	69.4	42.1
240	71.0	34.4
96 + Na_2SO_4*	66.0	80.0
128 + Na_2SO_4	70.1	63.8
160 + Na_2SO_4	72.4	52.7
192 + Na_2SO_4	73.1	44.3
240 + Na_2SO_4	73.3	35.6

*The average Na_2SO_4 dosage utilized was 51 kg Na/m^3.

these investigations. Therefore, during regeneration cycles, the NaCl solution was fed into the exhausted bed before the Na_2SO_4 waste brine in order to remove most of the calcium ions from the exchange resins, and thus decrease the $CaSO_4$ precipitation possibility during the subsequent injection of Na_2SO_4. In addition, a number of samples of regenerant waste effluent taken during the regeneration process showed that $CaSO_4$ precipitation did occur when all combinations of NaCl plus Na_2SO_4 were used. At dosages of 128, 160, 192, and 240 kg NaCl/m^3 (8, 10, 12, and 15 lb NaCl/ft^3) plus Na_2SO_4, no $CaSO_4$ precipitation occurred within the exchange bed, but a supersaturated solution was formed with delayed precipitation (30) occurring after the solution exited the bed. However, at a dosage of 96 kg NaCl/m^3 (6 lb NaCl/ft^3) plus Na_2SO_4, precipitation occurred in the bed causing the waste line to be plugged. This was because more calcium ions still remained on the exchange resins after this lower dosage of NaCl solution had passed through the bed. During the subsequent Na_2SO_4 regeneration, the high sulfate concentration in the Na_2SO_4 waste brine, plus the high density of calcium ions on the resin, caused higher concentrations of $CaSO_4$ to exist in the regenerant solution and a more rapid precipitation of $CaSO_4$ occurred within the bed. As a result of the $CaSO_4$ fouling situation encountered at 96 kg NaCl/m^3 (6 lb NaCl/ft^3) plus Na_2SO_4, no lower NaCl dosage plus Na_2SO_4 regeneration combinations were deemed feasible.

SUMMARY

The results obtained in these studies demonstrated that the coupled sodium-form ion exchanger and 4K RO unit was capable of high-recovery treatment of AMD at Crown, WV. When compared to the use of each treatment system separately, it was found that not only was the RO water recovery effectively enhanced by using IX pretreatment, but also NaCl regenerant savings were

realized with the aid of Na_2SO_4 waste brine discharged from the RO unit. Several points are worth noting.

- During the experiments with the coupled system, high water recoveries of 90-93 percent were maintained without membrane fouling by controlling the feed pressure to the reverse osmosis system at 550 to 625 psi. The limiting factor in recovery was $CaSO_4$ precipitation; however, the recoveries obtained do represent a significant increase over the recovery (about 50 percent) attainable by RO alone on Crown AMD.

- The product water obtained from this coupled system was capable of satisfying potable water standards except for the low value of pH (31), and is easily buffered to the proper limit. The higher concentrations of sodium and sulfate in the product water, when compared to the concentrations of other ions, can be explained by the lower rejections of the membranes for sodium (95 percent), and the existence of high concentrations of sodium and sulfate in the brine side when operating at recoveries of over 90 percent.

- The sodium-form strong-acid cation exchanger exhibited qualitatively the same hydrogen removal phenomena during the exhaustion process for the salt dosages utilized in this research. This is seen in the shapes of all FMA curves obtained, which are similar and independent of the amount of salt dosage used.

- A lower ion leakage, higher IX capacity, and higher regenerant utilization were obtained by using both NaCl and Na_2SO_4 waste brine dosages when compared to those obtained by only using the same amount of NaCl dosage. Thus, the Na_2SO_4 waste brine became an effective regenerant aid resulting in NaCl dosage savings of approximately 40 percent. In theory, the NaCl dosage savings will decrease with increasing salt dosages and finally reach zero savings as the asymptotic capacity is attained.

- An asymptotic hardness leakage, and an asymptotic capacity of 73.3 kg $CaCO_3/m^3$ (32.0 kgr $CaCO_3/ft^3$), were found to be approached around a salt dosage of 240 kg $NaCl/m^3$ (15 lb $NaCl/ft^3$) plus 51 kg Na/m^3 (3.2 lb Na/ft^3) of Na_2SO_4. A comparison of this asymptotic capacity to the resin-rated capacity of 80.2 - 82.4 kg $CaCO_3/m^3$ (35-36 kgr $CaCO_3/ft^3$) implies that resin degradation might have occurred during the course of the experiments as a result of resin fouling. In particular, iron fouling of resin sites is one possible explanation for this effect, although the data collected during the investigations did not allow a complete substantiation of the degree to which this might have occurred.

- Due to the severity of $CaSO_4$ precipitation within the bed during the Na_2SO_4 regeneration of the IX bed, a salt dosage of 6 lb $NaCl/ft^3$ plus Na_2SO_4 was the lower limit of investigation used in this research. At higher NaCl dosages plus Na_2SO_4, a supersaturated regenerant effluent was formed with delayed precipitation occurring outside the bed instead of precipitation occurring on the resin.

It is recommended that the following areas be investigated to better enhance and understand the potential of coupled IX/RO systems treatment of AMD:

- Membranes having high sodium rejection should be used to raise the sodium concentration in the waste brine to determine the effect of this increase upon the waste brine as a regenerant aid and simultaneously improve the product quality by decreasing sodium concentration.

- A determination of capacity as a function of time should be done at various NaCl dosages to find the degree of the resin degradation during long-term operations. This experiment would permit the quantification of fouling to be expected when dealing with the concentrations of iron encountered in this study.

- A study of counter-current coupled IX/RO systems should be made to examine the possiblity of increasing recovery due to the lower hardness leakage expected in the effluent of the ion exchanger. In addition, because most of calcium ions remained at the upper portion of the bed after a downward exhaustion process, the sulfate ions contained in the regenerant aid stream would not contact calcium ions until the stream passed through the upper portion of the bed during the upward regeneration process in a counter-current operation. Therefore, the residence time of the $CaSO_4$ solution in the bed would decrease, and the possibility of $CaSO_4$ fouling within the bed would diminish.

- Studies of precipitate inhibitor (e.g. sodium hexametaphosphate) additions to the Na_2SO_4 regenerant aid should be conducted to determine their effectiveness for preventing $CaSO_4$ precipitation within the IX resin bed.

- Further investigations should be made to determine the optimum (most economical) combinations of NaCl-Na_2SO_4 regenerant solutions, to evaluate the operational and cost effects attributable to reduced fluxes and elevated osmostic pressures occuring in high recovery coupled sodium cycle IX/RO operations, and to carefully document the problems and costs of the disposal of liquid wastes resulting from IX backwash, regeneration, and rinse operations.

- Additional studies should be implemented to develop a large-scale coupled IX/RO system to treat AMD waters at high RO unit recoveries, without having to recycle any portions of the concentrated brine. This would provide a more realistic model for the evaluation of the RO operating costs necessary for complete system economics.

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APPENDIX A

CHEMISTRY ANALYSES FOR 60K RO UNIT OPERATIONS (60 - 90 PERCENT RECOVERY)

TABLE A-1. 59.7 PERCENT UNIT RECOVERY

	Raw Feed	Blended Feed	Brine	Product	Percent Rejection[a]
Conductivity, μmhos/cm	3700	2800	6000	60	97.9
pH	3.7	2.9	2.7	4.5[b]	
Acidity (as $CaCO_3$ to end point pH 7.3) mg/l	640	510	1200	30	94.1
Ca, mg/l	400	220	480	1.8	99.2
Mg, mg/l	110	64	180	0.7	99.5
Total Fe, mg/l	260	150	370	1.7	98.9
Fe^{2+}, mg/l	240	140	350	<1.7	98.8
Na, mg/l	430	260	660	4.2	98.4
Al, mg/l	7.8	5.4	13.5	0.07	98.7
Mn, mg/l	4.0	2.6	5.5	0.05	99.1
SO_4, mg/l	2900	1800	4400	23	98.7
TDS, mg/l	4100	2600	6100	31	98.8

[a] $$\text{Percent Rejection} = \frac{\text{Blended Feed Conc. (mg/l)} - \text{Product Conc. (mg/l)}}{\text{Blended Feed Conc. (mg/l)}} \times 100\%$$

[b] Product pH exiting RO unit prior to recycle and acidification

TABLE A-2. 69.6 PERCENT UNIT RECOVERY

	Raw Feed	Blended Feed	Brine	Product	Percent Rejection[a]
Conductivity, µmhos/cm	3600	2200	6200	62	99.0
pH	4.0	2.6	2.2	3.1[b]	
Acidity (as $CaCO_3$ to end poiny pH 7.3) mg/l	740	460	1400	120	73.9
Ca, mg/l	310	120	430	1.7	98.5
Mg, mg/l	110	44	140	0.7	98.4
Total Fe, mg/l	320	130	450	2.5	98.1
Fe^{2+}, mg/l	290	120	380	1.6	98.7
Na, mg/l	480	180	620	4.2	97.7
Al, mg/l	33	27	52	0.04	99.9
Mn, mg/l	5.1	2.1	6.7	0.03	98.6
SO_4, mg/l	3300	2100	4400	55	97.4
TDS, mg/l	4500	2600	6100	64	97.5

TABLE A-3. 73.6 PERCENT UNIT RECOVERY
(7-4-3 ARRAY)

	Raw Feed	Blended Feed	Brine	Product	Percent Rejection[a]
Conductivity, µmhos/cm	3800	2400	6400	62	97.6
pH	4.3	2.8	2.5	4.2[b]	
Acidity (as $CaCO_3$ to end point pH 7.3) mg/l	830	470	1400	59	87.4
Ca, mg/l	360	130	550	1.8	98.6
Mg, mg/l	120	50	160	0.6	98.8
Total Fe, mg/l	330	150	420	1.8	98.8
Fe^{2+}, mg/l	320	130	410	1.1	99.2
Na, mg/l	520	250	640	4.5	98.2
Al, mg/l	6.5	3.0	8.9	0.14	95.3
Mn, mg/l	5.5	2.5	6.9	0.06	97.6
SO_4, mg/l	2900	1400	3900	27	98.1
TDS, mg/l	4200	2000	5700	36	98.2

[a] $$\text{Percent Rejection} = \frac{\text{Blended Feed Conc. (mg/l)} - \text{Product Conc. (mg/l)}}{\text{Blended Feed Conc. (mg/l)}} \times 100\%$$

[b] Product pH exiting RO unit prior to recycle and acidification

TABLE A-4. 73.6 PERCENT UNIT RECOVERY
(5-4-3-2 ARRAY)

	Raw Feed	Blended Feed	Brine	Product	Percent Rejection[a]
Conductivity, µmhos/cm	3650	2000	6200	50	97.5
pH	4.5	2.8	2.4	4.1[b]	
Acidity (as $CaCO_3$ to end point pH 7.3) mg/l	740	420	1300	50	88.1
Ca, mg/l	360	100	440	1.4	98.6
Mg, mg/l	110	38	290	0.4	98.9
Total Fe, mg/l	300	100	390	1.2	98.8
Fe^{2+}, mg/l	300	100	360	<1.2	98.8
Na, mg/l	470	180	620	3.6	98.0
Al, mg/l	2.5	1.0	3.4	0.03	97.0
Mn, mg/l	5.3	1.9	6.3	0.04	97.9
SO_4, mg/l	2700	1200	3600	17	98.6
TDS, mg/l	4000	1600	5300	23	98.6

TABLE A-5. 80.0 PERCENT UNIT RECOVERY

	Raw Feed	Blended Feed	Brine	Product	Percent Rejection[a]
Conductivity, µmhos/cm	4100	1950	6900	40	97.0
pH	4.2	2.9	2.4	3.8[b]	
Acidity (as $CaCO_3$ to end point pH 7.3) mg/l	910	400	1500	85	78.8
Ca, mg/l	400	76	510	1.0	98.7
Mg, mg/l	130	31	160	0.4	98.7
Total Fe, mg/l	340	80	430	1.7	97.9
Fe^{2+}, mg/l	330	76	400	1.6	98.2
Na, mg/l	510	150	610	3.0	97.0
Al, mg/l	4.6	1.1	6.1	0.04	96.4
Mn, mg/l	5.8	1.6	7.2	0.01	99.4
SO_4, mg/l	3200	800	4600	16.0	98.0
TDS, mg/l	4600	1100	6400	24	97.8

[a] $$\text{Percent Rejection} = \frac{\text{Blended Feed Conc. (mg/l)} - \text{Product Conc. (mg/l)}}{\text{Blended Feed Conc. (mg/l)}} \times 100\%$$

[b] Product pH exiting RO unit prior to recycle and acidification

TABLE A-6. 85.4 PERCENT UNIT RECOVERY

	Raw Feed	Blended Feed	Brine	Product	Percent Rejection[a]
Conductivity, μmhos/cm	4800	1600	7800	180	97.9
pH	4.2	2.9	2.4	3.9[b]	
Acidity (as $CaCO_3$ to end point pH 7.3) mg/l	920	380	1600	92	75.8
Ca, mg/l	390	55	430	0.9	98.4
Mg, mg/l	120	18	150	0.3	98.3
Total Fe, mg/l	350	51	380	1.4	97.3
Fe^{2+}, mg/l	340	47	340	1.1	97.7
Na, mg/l	510	96	550	2.3	97.6
Al, mg/l	9.7	1.9	11	0.08	95.8
Mn, mg/l	5.4	1.0	5.9	0.02	98.0
SO_4, mg/l	3300	1000	4200	16	98.4
TDS, mg/l	4500	1300	5500	21	98.4

TABLE A-7. 90.3 PERCENT UNIT RECOVERY

	Raw Feed	Blended Feed	Brine	Product	Percent Rejection[a]
Conductivity, μmhos/cm	4100	1320	9250	58	95.6
pH	5.2	2.5	2.1	4.2[b]	
Acidity (as $CaCO_3$ to end point pH 7.3) mg/l	920	320	1600	92	71.3
Ca, mg/l	370	36	450	0.7	98.1
Mg, mg/l	130	14	160	0.3	97.9
Total Fe, mg/l	340	35	440	0.1	99.7
Fe^{2+}, mg/l	330	32	440	0.1	99.7
Na, mg/l	580	76	700	2.4	96.8
Al, mg/l	8.5	0.9	9.6	0.02	97.8
Mn, mg/l	6.0	0.8	7.3	0.04	95.0
SO_4, mg/l	3300	720	5200	14	98.1
TDS, mg/l	4700	880	7000	17	98.1

[a] $$\text{Percent Rejection} = \frac{\text{Blended Feed Conc. (mg/l)} - \text{Product Conc. (mg/l)}}{\text{Blended Feed Conc. (mg/l)}} \times 100\%$$

[b] Product pH exiting RO unit prior to recycle and acidification

APPENDIX B

NEUTROLOSIS PROCESS MODEL

MODEL DERIVATION

Flow, Concentration, and Parametric Relations

Figure B-1 shows a schematic flowsheet for the neutrolosis process. Using the flow stream variables indicated in Figure B-1, the following stream and mass balances can be written:

$$F_f + F_r = F_c \tag{B1}$$

$$F_b + F_p = F_c \tag{B2}$$

$$F_s + F_r = F_b \tag{B3}$$

$$F_rC_r + F_fC_f = F_cC_c \tag{B4}$$

$$F_cC_c \simeq F_bC_b{}^* \tag{B5}$$

Define the following parameters:

$$\text{Overall Recovery} \quad \nu \equiv F_p/F_f \tag{B6}$$

$$\text{Unit Recovery} \quad \alpha \equiv F_p/F_c \tag{B7}$$

$$\text{Sludge Out Ratio} \quad \beta \equiv F_s/F_b \tag{B8}$$

$$\text{Recycle Ratio} \quad R \equiv F_r/F_f. \tag{B9}$$

Rearranging Equation (B5) and using Equation (B4),

$$C_b = C_c \frac{F_c}{F_b} = C_r \frac{F_r}{F_b} + C_f \frac{F_f}{F_b}, \tag{B10}$$

which gives

$$C_b = \frac{F_f}{F_b} \left(\frac{F_r}{F_f} C_r + C_f \right), \tag{B11}$$

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*Assumes $C_p \simeq 0$ which is valid for high rejection membranes.

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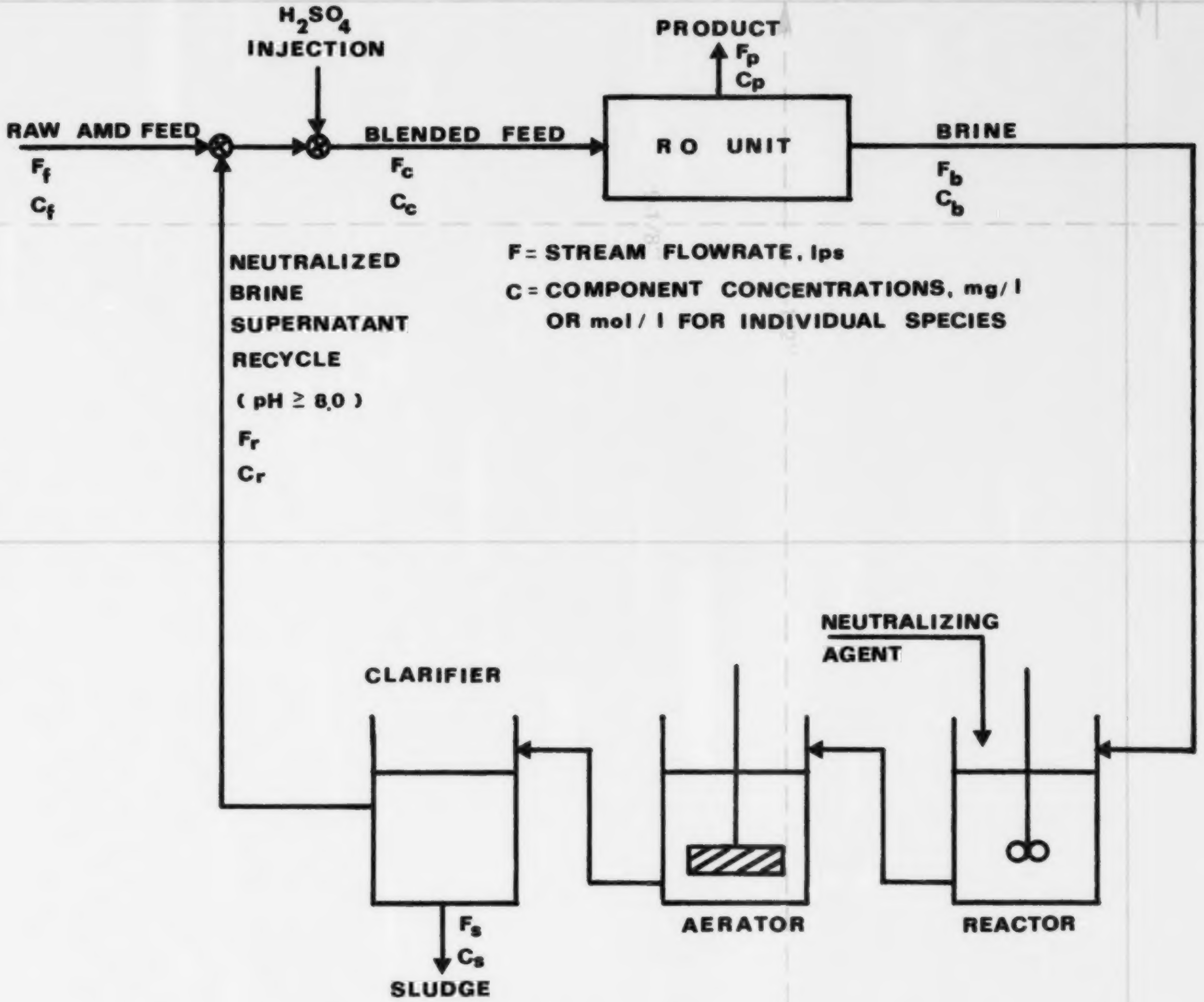
H_2SO_4 INJECTION
RAW AMD FEED
F_f
C_f
BLENDED FEED
F_c
C_c
PRODUCT
F_p
C_p
R O UNIT
BRINE
F_b
C_b
F = STREAM FLOWRATE, lps
C = COMPONENT CONCENTRATIONS, mg/l OR mol/l FOR INDIVIDUAL SPECIES
NEUTRALIZED BRINE SUPERNATANT RECYCLE
(pH ≥ 8.0)
F_r
C_r
NEUTRALIZING AGENT
CLARIFIER
AERATOR
REACTOR
F_s
C_s
SLUDGE

Figure B-1. Schematic of the neutrolosis process.

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

or

$$C_b = \frac{F_f}{F_b} (R\ C_r + C_f) , \qquad \text{(B12)}$$

when the definition of R in Equation (B9) is used.

Rearranging Equation (B3) gives,

$$\frac{F_s}{F_b} + \frac{F_r}{F_b} = 1, \qquad \text{(B13)}$$

and using Equation (B8) which defines β,

$$\beta + \frac{F_r}{F_f} \cdot \frac{F_f}{F_b} = 1. \qquad \text{(B14)}$$

Upon substitution of R from Equation (B9), Equation (B14) becomes,

$$\beta + R \frac{F_f}{F_b} = 1. \qquad \text{(B15)}$$

This last expression can be rearranged as

$$\frac{F_f}{F_b} = \frac{1 - \beta}{R} , \qquad \text{(B16)}$$

which can be substituted into Equation (B12) to yield,

$$C_b = \frac{1 - \beta}{R} (R\ C_r + C_f), \qquad \text{(B17)}$$

or

$$C_b = (1 - \beta)\ C_r + \frac{(1 - \beta)}{R} C_f. \qquad \text{(B18)}$$

Employing Equations (B16), (B1), (B2), and (B3),

$$\frac{1 - \beta}{R} = \frac{F_f}{F_b} = \frac{F_s/F_b}{F_s/F_f} = \frac{F_s/F_b}{(F_f - F_p)/F_f}, \qquad \text{(B19)}$$

or

$$\frac{1 - \beta}{R} = \frac{\beta}{1 - \nu} , \qquad \text{(B20)}$$

when the definition of ν from Equation (B6) is utilized.

Rearranging Equation (B20),

$$R = (1 - \nu)\left(\frac{1 - \beta}{\beta}\right) , \qquad \text{(B21)}$$

and upon substituting Equation (B20) into Equation (B18),

$$C_b = (1 - \beta)\, C_r + \frac{\beta}{1 - \nu}\, C_f. \tag{B22}$$

Another useful relation can be obtained by using Equation (B2) and the definition of α from Equation (B6) to write,

$$\frac{F_b}{F_c} + \frac{F_p}{F_c} = 1 = \frac{F_b}{F_c} + \alpha, \tag{B23}$$

which can be combined with Equation (B1) to give

$$\alpha = 1 - \frac{F_b}{F_f + F_r}. \tag{B24}$$

Upon substituting Equation (B3) into the above expression, the result is,

$$\alpha = 1 - \frac{F_s + F_r}{F_f + F_r}. \tag{B25}$$

This last relation can be rearranged as

$$\alpha = 1 - \frac{F_s/F_f + F_r/F_f}{1 + F_r/F_f}, \tag{B26}$$

which becomes

$$\alpha = \frac{1 + R + \nu - 1 - R}{1 + R} \tag{B27}$$

when Equations (B1), (B2), (B3), (B6) and (B9) are used, or

$$\alpha = \frac{\nu}{1 + R}. \tag{B28}$$

Combining Equations (B21) and (B28) to eliminate R, then yields

$$\nu = \frac{\alpha}{\beta + \alpha(1 - \beta)}. \tag{B29}$$

Calcium Sulfate and Metallic Hydroxide Solubility Calculations

Calcium Sulfate--

The solubility product of calcium sulfate in a solution with other solutes can be determined from ionic interference considerations as follows:

$$Ksp = 1.8 \times 10^{-3}\, (I)^{3/4}\, (\text{moles/liter})^2, \tag{B30}$$

where

$$I = 1/2 \sum_i C_i\, Z_i^2, \tag{B31}$$

with C_i the molar concentration (moles/liter) of species i, and Z_i the valence of species i.

A saturation factor (SF) can be defined for calcium sulfate as

$$SF = \sqrt{\frac{[Ca]\ [SO_4]}{Ksp}}\ , \tag{B32}$$

or

$$SF = \sqrt{\frac{[Ca]\ [SO_4]}{1.8 \times 10^{-3}\ (I)^{3/4}}}\ , \tag{B33}$$

where [Ca] and $[SO_4]$ are the molar concentrations of calcium and sulfates respectively.

This relation can be used either to determine the potential for calcium sulfate precipitation from a given solution, or it can be modified further to allow determination of the maximum allowable recovery in an RO unit before precipitation occurs on the membranes at an appreciable rate. This requires knowledge of the brine concentrations, C_b, or a relationship such as Equation (3) which gives

$$C_b \simeq C_f/(1 - \nu)\ , \tag{B34}$$

where C_f and ν have been defined previously.

Upon substitution of this relation into Equations (B31) and (B33), the following equation is obtained for the saturation factor of calcium sulfate in the brine based upon calcium and sulfate concentrations in the feed, and the desired overall recovery:

$$SF \simeq \sqrt{\frac{[Ca]_f\ [SO_4]_f}{1.8 \times 10^{-3}\ (I_f)^{3/4}}} \left(\frac{1}{1 - \nu}\right)^{5/8}\ . \tag{B35}$$

Equation (B35) was utilized to develop Figure B-2.

Metal Hydroxides--

Metal solubility in the neutrolosis process was determined from hydroxide solubility product considerations using

$$Ksp = [M][OH]^Z\ , \tag{B36}$$

where Z is the metal valence and the concentrations are in moles/liter. The metal concentration can then be determined by

$$[M] = Ksp/[OH]^Z\ . \tag{B37}$$

Thus, by specifying the pH the [OH] concentration is known, and [M] can be determined provided Ksp is given, e.g. as in TABLE B-1.

TABLE B-1. Ksp VALUES

Component	Z	Ksp*
Mg	2	9×10^{-12}
Al	3	1×10^{-15}**
Mn	2	8×10^{-14}
Fe^{+3}	3	6×10^{-38}

*Approximate at 25°C.

**Al is amphoteric and may resolubilize at a pH > 9.0.

The model equations derived have been used to construct the plots shown in Figures B-2 through B-4. The procedure used, which would permit lime neutrolosis performance analyses to be made for a spectrum of AMD feed qualities beyond the illustrative cases presented, is as follows:

1) Equation (B22) is used to determine the brine concentrations for each component. The feed concentrations, C_f's, are specified, but the recycle stream concentrations must be obtained. If the solubility of a given component is low enough so that the recycle stream is saturated with that component, then C_r is equal to the solubility of that component. If the solubility is not limiting as to the concentration of a component, then $C_r \simeq C_f/(1 - \nu)$. This procedure is applicable to all the cations except for calcium.

2) For the case of calcium, C_r may be equal to the solubility concentration if the recycle stream is saturated in calcium sulfate. However, if the recycle stream is not saturated, then C_r must be determined from

$$C_r = \frac{C_f}{1 - \nu} + \frac{C_{b'}}{\beta} , \qquad \text{(B38)}$$

where $C_{b'}$ is the additional concentration of calcium in the supernatant due to lime addition.

3) The calculated brine concentrations are used with the ionic interference method of determining calcium sulfate solubility to compute the saturation factor (SF).

4) The parameters β and ν are varied so as to determine the saturation factor SF = f (β, ν), with the results shown graphically in the plots such as Figures B-3 and B-4.

5) The constant unit recovery lines on the plots are determined from equation (B29).

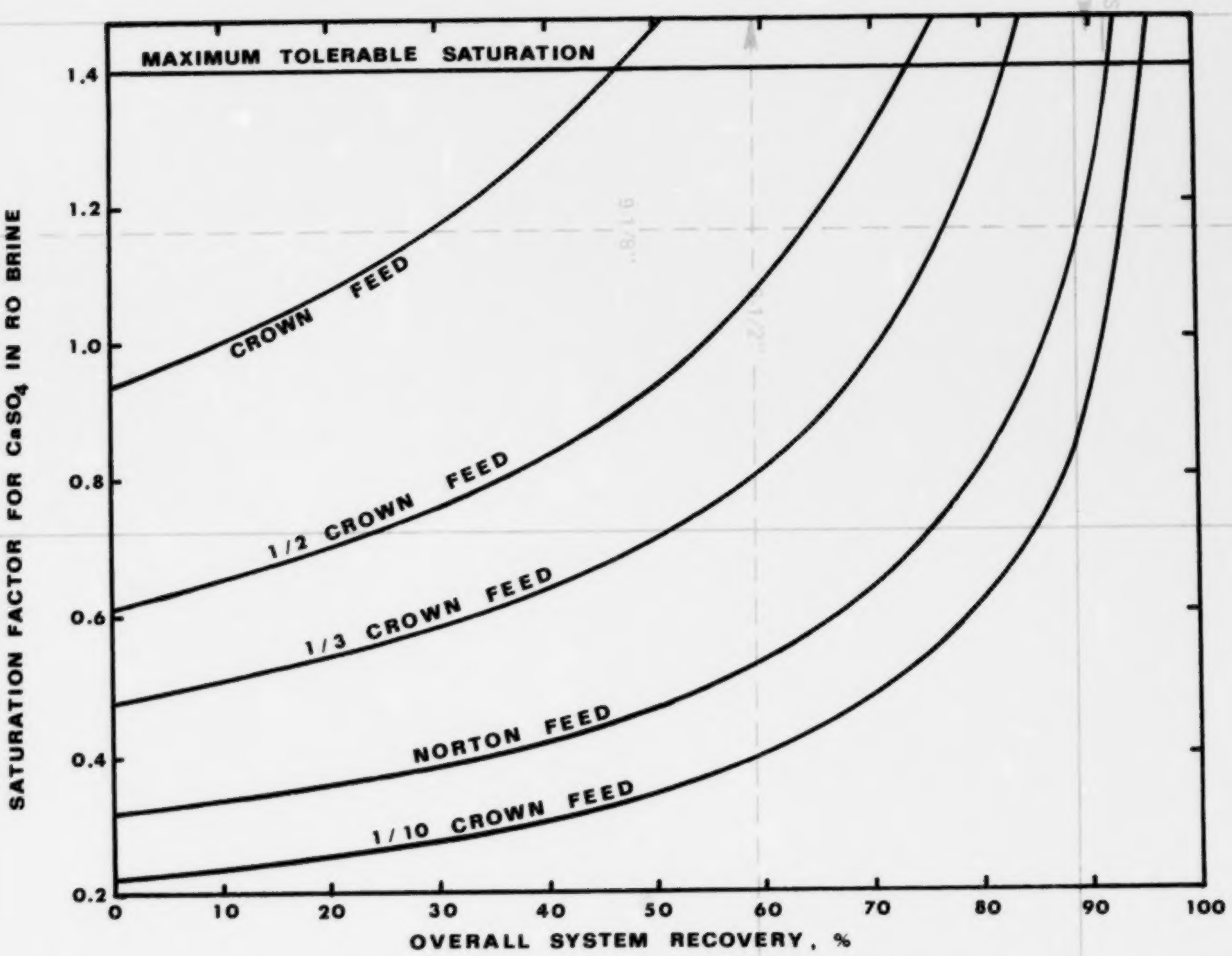

Figure B-2. $CaSO_4$ saturation factor versus once-through RO recovery for several AMD strengths.

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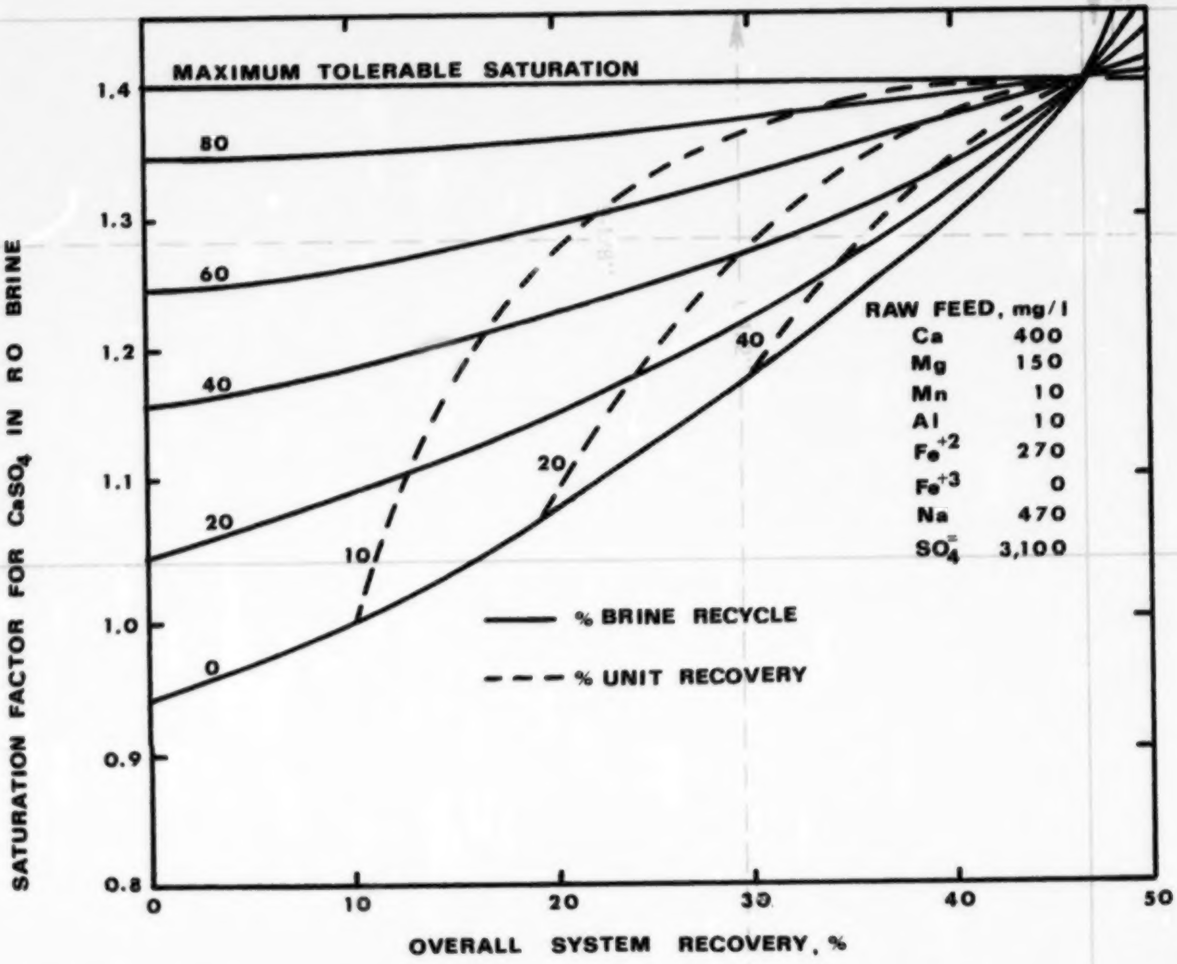

Figure B-3. Lime neutrolosis of Crown AMD to pH 11.

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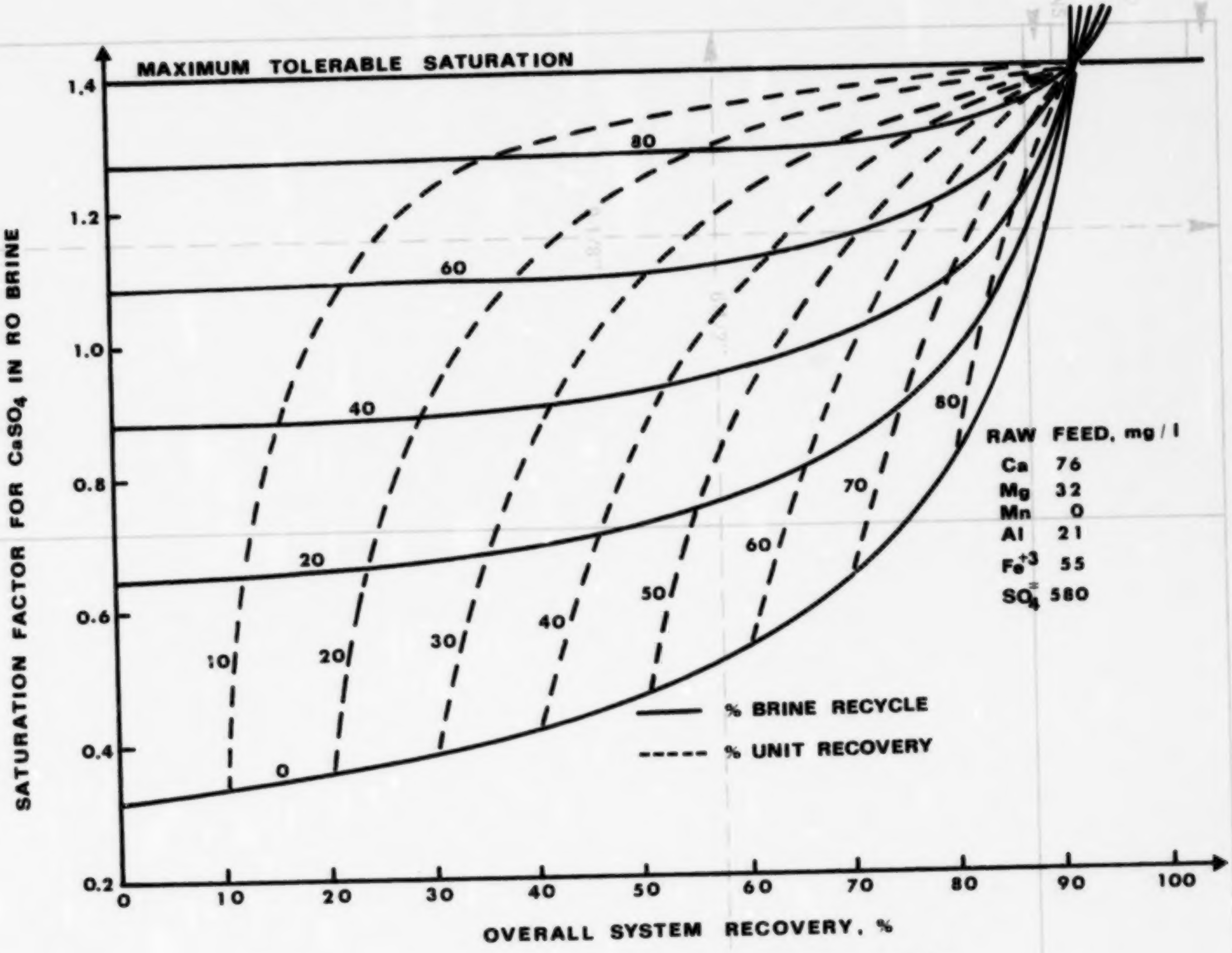

Figure B-4. Lime neutrolosis of Norton type AMD to pH 11.

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MODEL UTILIZATION

Figure B-2 shows the once-through recovery performance of RO for a spectrum of AMD feeds varying from the maximum strength of Crown AMD down to a feed containing one-tenth the constituent concentrations of Crown water. Note that the mine drainage feed utilized at EPA's Norton Field Site (5) lies between the strengths of one-tenth and one-third Crown AMD. The important points lie along the 1.4 $CaSO_4$ saturation line, showing for example that the highest once-through recovery to be expected for Crown AMD is approximately 47 percent, whereas it is 74 percent for half-strength Crown feed, about 91.5 percent for Norton AMD, etc. These calculated maximum once-through recoveries agree quite well with experimental observations.

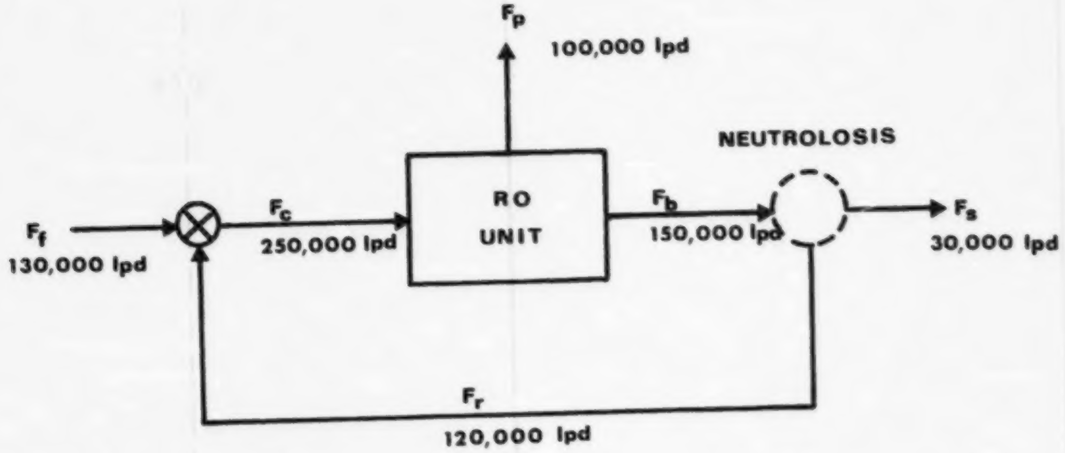
Figures B-3 and B-4 display the expected RO system performance for neutrolosis modes of operation with the brine neutralized to pH 11 levels for Crown and Norton type AMD. Two sets of parametric curves appear on each figure. The solid lines represent operating conditions of constant brine recycle ratio, R, whereas the dashed lines represent plots of constant unit recovery, α. The lines of "zero" brine recycle are the once-through plots shown in Figure B-2; and it is seen that lines of a given unit recovery intersect the once-through recovery line at an identical overall system recovery point, as expected. In constructing these plots, considerations are given to the solubilities of the various ionic species in the neutralized brine at a pH value of 11, and in the blended feeds to the RO system, via chemical equilibrium calculations. The graphs are universal in the sense that they are independent of the capacity of the RO or neutrolosis system under study--and depend only on the strength of the raw AMD feed, pH neutralization level of the brine, and the ratio of various flow rates expressed as overall system recovery (ν), unit recovery, (α), and brine recycle ratio (R).

The graphs should be utilized only within permissible regions of operation for a given RO system. For example, the "permissible region" of Figure B-3 for the 60K RO unit is bounded on the right by the once-through recovery line, on the left by the 40 percent unit recovery line, and at the top by maximum $CaSO_4$ saturation line of 1.4. It is evident that we cannot go to the right of the once-through recovery line for the Crown AMD feed, nor can we operate above the 1.4 saturation factor in the brine without risking fouling in the last bank of modules. The lower limit of recovery in the 8-6 pressure vessel configuration of the 60K RO unit at Crown is essentially 40 percent in order to maintain acceptable brine to product flow ratios. Presumably, if all 14 pressure vessels of the Crown 60K RO unit were hooked in parallel in a single bank, a lower limit for the unit recovery could be established in the neighborhood of 20 percent. Note that for inherently weaker AMD, the permissible regions of operation are enlarged.

There is one additional item to note before proceeding with several case studies utilizing Figure B-4. Equilibrium concentrations of the ions have been assumed in all streams at the various pH levels. This is not truly correct, since it has been experimentally observed, for example, that calcium ion concentrations in neutralized waste brine may be the order of 1000-1100 mg/l, which exceeds the equilibrium value even at the 1.4

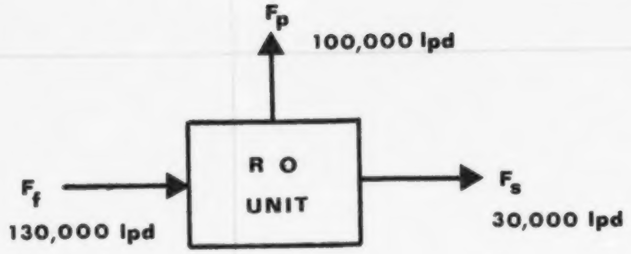
saturation factor level. It is possible to have $CaSO_4$ in this excessively supersaturated state; however, in actual operations gypsum crystal formation is noted on the surfaces of clarifiers, filters, and RO membranes. In essence, these surfaces act as "catalytic sites" to drive the solution toward equilibrium, which is unfortunate for the operation, since the precipitation occurs on surfaces that need to be permeable. In any event, the graphs are based on equilibrium $CaSO_4$ concentrations, which is an optimistic assumption compared to the actual situations encountered. However, this ideal assumption does not make a strong case for neutrolosis as indicated in the three simple case studies which follow.

Consider the design basis of an RO unit to be a 100,000 lpd permeate flow rate produced from Norton type AMD with brine neutralization to a pH 11. In this illustration, the product flow will remain constant. This constant product flow mode is felt to be the most realistic type application since RO normally is too expensive to treat an entire AMD waste flow. Select, for example, an operating point of 40 percent unit recovery and 80 percent brine recycle for a neutrolosis process. Figure B-4 shows that the overall system recovery is approximately 77 percent and the $CaSO_4$ saturation factor in the brine is approximately 1.3. The flow diagram for the process is:



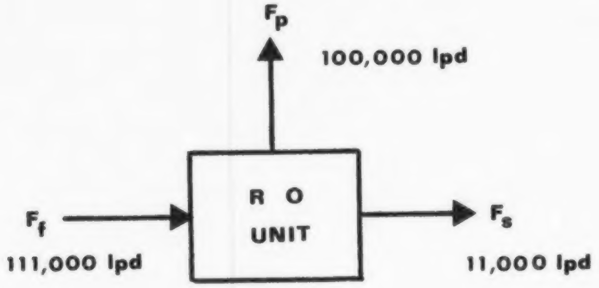
NOTE: At pH 11, essentially all ions except calcium and sodium are precipitated at equilibrium conditions.

Now note that a once-through recovery of 77 percent could also be achieved at a $CaSO_4$ brine saturation factor of 0.75, which is well-below any potential for fouling. In this case the flow schematic is:



F_p
100,000 lpd
R O UNIT
F_f
130,000 lpd
F_s
30,000 lpd

On the other hand, if the process could have been run with a $CaSO_4$ brine saturation factor of 1.3, the process could be operated at a once-through recovery of 90 percent.



F_p
100,000 lpd
R O UNIT
F_f
111,000 lpd
F_s
11,000 lpd

It appears from these three elementary illustrations that once-through operations have advantages over the neutrolosis case. The first is that a once-through operation can produce the same output as the neutrolosis case with absolutely no danger of gypsum fouling of the membranes. The feed volume to the RO unit is also much less for the once-through case which means a greatly reduced pumping cost.

The "optimal" once through system operates near the maximum permissible brine saturation factor. It is seen in this case that the pumping requirements are even further reduced due to the smaller feed volume, although there is some counter effect due to increase osmotic pressure. The waste flow is approximately a third of that produced in the neutrolosis case. Similar results will occur independent of the strength of AMD is utilized, i.e. the once-through case will always appear to have an advantage for a given desired product output.